

Supporting Information

Copper-Mediated Cascade C-H/N-H Annulation of Indolocarboxamides with Arynes: Construction of Tetracyclic Indoloquinoline alkaloids

Ting-Yu Zhang,[†] Chang Liu,[†] Chao Chen,[†] Jian-Xin Liu,[§] Heng-Ye Xiang,[§] Wei Jiang,^{||} Tong-Mei Ding[†] and Shu-Yu Zhang^{*†‡||}

[†]School of Chemistry and Chemical Engineering, [‡]Sixth People's Hospital South Campus, and [§]Zhiyuan College, Shanghai Jiao Tong University, Shanghai, 200240, P. R. China.

^{||}School of Chemistry & Environmental Engineering, International Healthcare Innovation Institute, Wuyi University, Jiangmen, 529020, P. R. China.
E-mail: zhangsy16@sjtu.edu.cn

Contents

1. General information	S1
2. General procedures for the preparation of substrates	S1
3. Experimental details and characterization data	S11
4. General procedures for Cu-mediated C-H Annulation reactions	S14
5. Substrate scope of the Cu-mediated C-H annulation reactions	S15
6. X-Ray crystallographic analysis of 4 and 28	S26
7. Applications of copper-mediated C-H/N-H annulation in the construction of <i>Tetracyclic Indoloquinoline alkaloids</i>	S31
8. Preliminary mechanistic studies	S33
9. References	S36
10. Copies of ¹ H and ¹³ C NMR spectra	S37

1. General information

Solvents: Dichloromethane was distilled from CaH₂ and other solvents used in this manuscript were purchased in anhydrous form.

Reagents: All commercial materials, purchased from Aldrich, Adamas, Alfa Aesar, energy, TCI and Acros, were used as received unless otherwise noted. Cu(OAc)₂ (99.99%, Aldrich), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (97%, Energy), tetrabutylammonium iodide (TBAI) (98%, Energy) and cesium fluoride (CsF) (98%, Energy) were used in the Cu-mediated annulation reactions.

Reactions: All reactions were performed in oven-dried glassware under an atmosphere of oxygen unless otherwise noted. All yields reported were averages of at least three experimental runs.

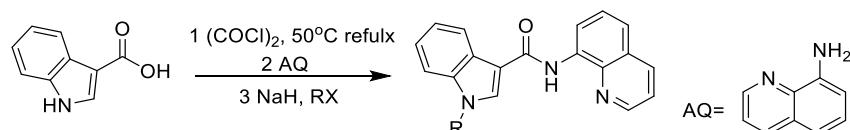
Chromatography: Thin layer chromatography (TLC) was carried out on silica gel 60 F254 pre-coated glass plates. Visualization was detected by irradiation with UV light (254 nm), or by treatment with a solution of phosphomolybdic acid in ethanol followed by heating. Flash chromatography was carried out on 200 – 300 mesh silica gel, eluting with a mixture of petroleum ether (b.p. 60 – 90 °C), ethyl acetate and dichloromethane.

NMR Spectroscopic: ¹H NMR and ¹³C NMR spectra were recorded on a Bruker AVANCE III HD 400 spectrometer, operating at 400 MHz and 100 MHz respectively. Chemical shifts (δ) were given in parts per million (ppm), and referenced relative to residual solvent CHCl₃ (7.26 ppm) in CDCl₃, or tetramethylsilane (0.00 ppm) as an internal standard for ¹H NMR spectra and deuterated solvent CDCl₃ (77.16 ppm) for ¹³C NMR spectra. Coupling constants (J) were reported in hertz (Hz). The following abbreviations are used to indicate the multiplicity of the signals: s = singlet, d = doublet, t = triplet, m = multiplet, and associated combinations, e.g. dd = doublet of doublets.

Mass Spectrometry: High resolution mass spectra (HRMS) were obtained on a Bruker Daltonics SolariX 7.0 Tesla Fourier Transform Ion Cyclotron Resonance (FT-ICR) Mass Spectrometer using the electrospray ionization (ESI) technique.

2. General procedures for the preparation of substrates

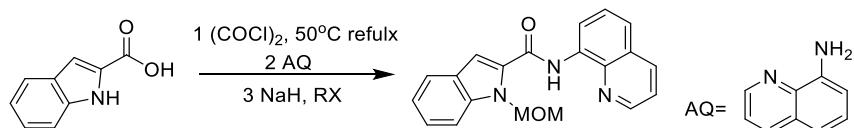
General procedure A:



According to literature procedure [1], 1*H*-indole 3-carboxylic acid (2 mmol) was heated at 50°C in oxalyl chloride (2 mL) for 1 h. The oxalyl chloride was then evaporated and the resulting solid was dissolved in anhydrous DCM (3 mL). The reaction was cooled in ice bath and 8-aminoquinoline (5 mmol) which dissolved in 3 mL DCM was added. The mixture was warmed to room temperature and stirred overnight after addition. Water (100 mL) was afterwards added and reaction mixture was extracted DCM (30 mL × 3). The organic layer was washed with a solution of HCl 10% (30 mL × 3), dried over anhydrous Na₂SO₄, filtered and concentrate in

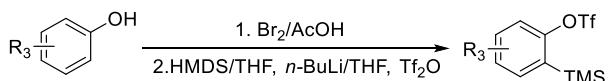
vacuum. The resulting residue was purified by flash column chromatography to give the amide. The amide was dissolved in THF (6 mL) was added in NaH (3 mmol) which dissolved in THF (9 mL) at 0°C. After addition, the mixture was warmed to room temperature and stirred for 1 h. The reaction was cooled in ice bath again and RX (3 mmol) was added. The solvent THF was then evaporated and the resulting solid was dissolved in chloroform (30 mL) and water (20 mL × 3) was afterwards added. The organic layer was dried over anhydrous Na₂SO₄, filtered and concentrate in vacuum. The resulting residue was purified by flash column chromatography to give the corresponding amide.

General procedure B:



According to literature procedure [1], 1*H*-indole 3-carboxylic acid (2 mmol) was heated at 50°C in oxalyl chloride (2 mL) for 1 h. The oxalyl chloride was then evaporated and the resulting solid was dissolved in anhydrous DCM (3 mL). The reaction was cooled in ice bath and 8-aminoquinoline (5 mmol) which dissolved in 3 mL DCM was added. The mixture was warmed to room temperature and stirred overnight after addition. Water (100 mL) was afterwards added and reaction mixture was extracted DCM (30 mL × 3). The organic layer was washed with a solution of HCl 10% (30 mL × 3), dried over anhydrous Na₂SO₄, filtered and concentrate in vacuum. The resulting residue was purified by flash column chromatography to give the amide. The amide was dissolved in THF (6 mL) was added in NaH (3 mmol) which dissolved in THF (9 mL) at 0°C. After addition, the mixture was warmed to room temperature and stirred for 1 h. The reaction was cooled in ice bath again and RX (3 mmol) was added. The solvent THF was then evaporated and the resulting solid was dissolved in chloroform (30 mL) and water (20 mL × 3) was afterwards added. The organic layer was dried over anhydrous Na₂SO₄, filtered and concentrate in vacuum. The resulting residue was purified by flash column chromatography to give the corresponding amide.

General procedure C:

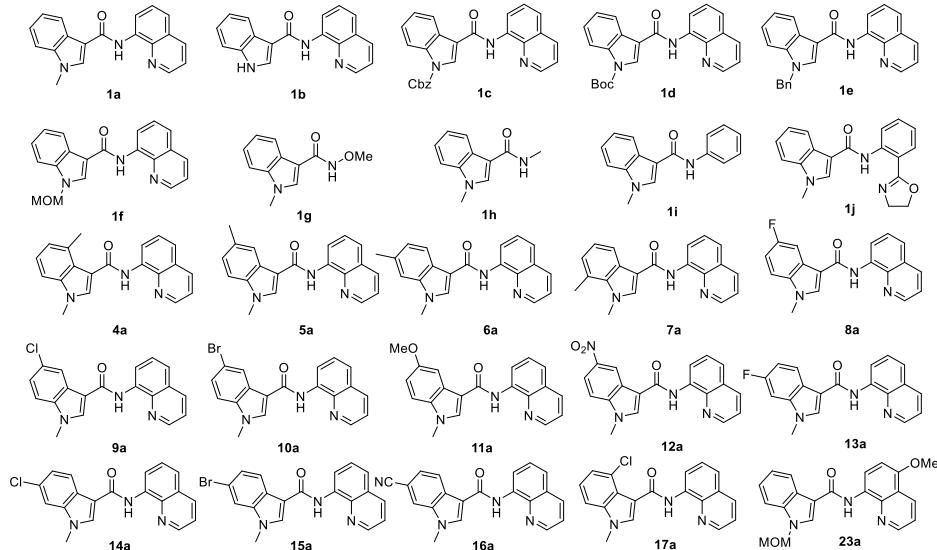


According to literature procedure [2], to a solution of phenol (21.7 mmol) in AcOH (7 mL) was added a solution of bromine (1.0 mL, 19.4 mmol) in AcOH (4 mL) dropwise at 0 °C and the reaction mixture was stirred for 30 min at this temperature. This mixture was poured into ice and filtered off. The residual solid was washed with water and dried to afford product 2-bromophenol. To a solution of 2-bromophenol (5.58 mmol) in THF (20 mL) was added HMDS (1.2 mL, 5.65 mmol) under argon atmosphere. The reaction mixture was refluxed for 2 h. After cooling to room temperature, the solvent was removed in vacuo. The residue was dissolved in THF (30 mL) under argon atmosphere and cooled to -78 °C. To the solution was added n-butyllithium (2.17 mmol, 2.4 M solution in hexane) dropwise. After stirring at -78 °C for 1.5 h, Tf₂O (0.98 mL 58.4 mmol) was added to reaction mixture dropwise at -78 °C. After stirring at -78 °C for 2 h, the reaction mixture was quenched with sat. NaHCO₃ aq. At -78 °C and this mixture was warmed to room temperature. The layers were separated, and then the aqueous layer was extracted with Et₂O three times. The combined organic layers were dried over Na₂SO₄. The solvent was removed in vacuo, and the residue was purified by silica gel column chromatography with

hexane to afford 2-(trimethylsilyl)phenyl trifluoromethanesulfonate as a colorless liquid.

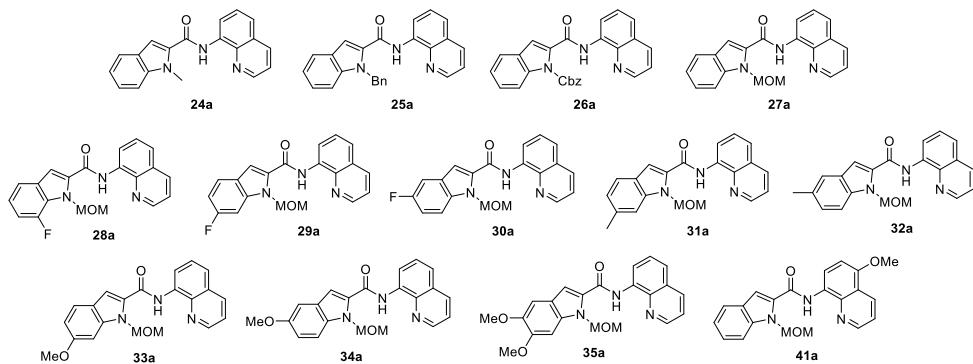
All these amides used are known compounds and were list as follows:

1) The substrates of amides **1a**^[3], **1b**, **1c**, **1d**, **1e**, **1f**, **1g**^[4], **1h**^[5], **1i**^[6], **1j**, **4a**, **5a**, **6a**, **7a**, **8a**, **9a**, **10a**, **11a**, **12a**, **13a**, **14a**, **15a**, **16a**, **17a** and **23a** were prepared according to the general procedure A.



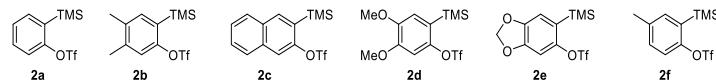
Scheme S1 Substrates of amides prepared according to the general procedure A

2) The substrates of amides **24a**^[7], **25a**, **26a**, **27a**, **28a**, **29a**, **30a**, **31a**, **32a**, **33a**, **34a**, **35a** and **43a** were prepared according to the general procedure B.

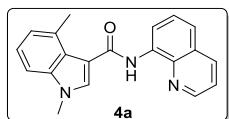


Scheme S2 Substrates of amides prepared according to the general procedure B

3) The substrates of benzyne precursors **2a**, **2b**, **2c**, **2d** and **2g** were purchased from TCI, and benzyne precursors **2e**^[2a] and **2f**^[2b] were prepared according to the general procedure C.

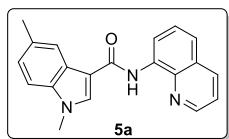


Scheme S3 Substrates of benzyne precursors



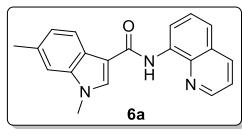
$R_f = 0.50$, 25 % EtOAc in hexanes

Prepared according to general procedure A. Purification of the crude product by flash column chromatography afforded the amide **4a** as white solid. **1H NMR** (CDCl_3 , 400 MHz, ppm): δ 10.22 (s, 1 H), 8.94 (dd, $J = 7.6, 1.1$ Hz, 1 H), 8.78 (dd, $J = 4.2, 1.6$ Hz, 1 H), 8.17 (dd, $J = 8.3, 1.6$ Hz, 1 H), 7.69 (s, 1 H), 7.59 (t, $J = 7.9$ Hz, 1 H), 7.51 (dd, $J = 8.2, 1.1$ Hz, 1 H), 7.44 (dd, $J = 8.3, 4.2$ Hz, 1 H), 7.26-7.21 (m, 2 H), 7.05 (dd, $J = 5.9, 1.3$ Hz, 1 H), 3.85 (s, 3 H), 2.80 (s, 3 H); **13C NMR** (CDCl_3 , 100 MHz, ppm) δ 164.4, 148.2, 138.7, 137.7, 136.5, 135.5, 132.5, 131.5, 128.2, 127.7, 125.0, 123.2, 123.2, 121.7, 121.1, 116.3, 114.1, 107.4, 33.5, 21.2; **HRMS**: calculated for $\text{C}_{20}\text{H}_{18}\text{N}_3\text{O}$ [$\text{M}+\text{H}^+$]: 316.1450; **found**: 316.1462.



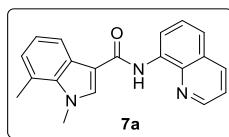
$R_f = 0.50$, 25 % EtOAc in hexanes

Prepared according to general procedure A. Purification of the crude product by flash column chromatography afforded the amide **5a** as white solid. **1H NMR** (CDCl_3 , 400 MHz, ppm): δ 10.56 (s, 1 H), 8.96 (dd, $J = 7.6, 1.1$ Hz, 1 H), 8.90 (dd, $J = 4.2, 1.6$ Hz, 1 H), 8.32 (s, 1 H), 8.19 (dd, $J = 8.3, 1.6$ Hz, 1 H), 7.88 (s, 1 H), 7.60 (t, $J = 7.9$ Hz, 1 H), 7.52-7.47 (m, 2 H), 7.30 (d, $J = 8.4$ Hz, 1 H), 7.18 (d, $J = 8.4$ Hz, 1 H), 3.88 (s, 3 H), 2.59 (s, 3 H); **13C NMR** (CDCl_3 , 100 MHz, ppm) δ 163.5, 148.2, 138.8, 136.5, 136.0, 135.6, 133.1, 131.4, 128.2, 127.8, 125.9, 124.4, 121.7, 120.84, 120.80, 116.3, 111.4, 109.9, 33.6, 21.9; **HRMS**: calculated for $\text{C}_{20}\text{H}_{18}\text{N}_3\text{O}$ [$\text{M}+\text{H}^+$]: 316.1450; **found**: 316.1459.



$R_f = 0.50$, 25 % EtOAc in hexanes

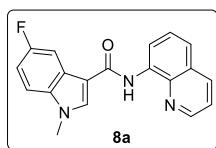
Prepared according to general procedure A. Purification of the crude product by flash column chromatography afforded the amide **6a** as white solid. **1H NMR** (CDCl_3 , 400 MHz, ppm): δ 10.53 (s, 1 H), 8.96 (dd, $J = 7.6, 1.2$ Hz, 1 H), 8.89 (d, $J = 4.2$ Hz, 1 H), 8.34 (d, $J = 8.2$ Hz, 1 H), 8.18 (d, $J = 8.3$ Hz, 1 H), 7.85 (s, 1 H), 7.59 (t, $J = 7.9$ Hz, 1 H), 7.51-7.46 (m, 2 H), 7.22 (d, $J = 8.3$ Hz, 1 H), 7.20 (s, 1 H), 3.85 (s, 3 H), 2.54 (s, 3 H); **13C NMR** (CDCl_3 , 100 MHz, ppm) δ 163.5, 148.3, 138.8, 138.0, 136.5, 135.5, 132.8, 128.2, 127.8, 123.7, 123.4, 121.7, 120.9, 120.5, 116.3, 111.8, 110.2, , 33.5, 21.9; **HRMS**: calculated for $\text{C}_{20}\text{H}_{18}\text{N}_3\text{O}$ [$\text{M}+\text{H}^+$]: 316.1450; **found**: 316.1454.



$R_f = 0.50$, 25 % EtOAc in hexanes

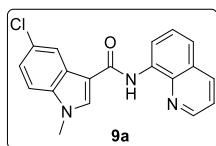
Prepared according to general procedure A. Purification of the crude product by flash column chromatography afforded the amide **7a** as white solid. **1H NMR** (CDCl_3 , 400 MHz, ppm): δ 10.46 (s, 1 H), 8.94 (dd, $J = 7.7, 1.1$ Hz, 1 H), 8.84 (dd, $J = 4.2, 1.6$ Hz, 1 H), 8.31 (d, $J = 8.1$ Hz, 1 H), 8.14 (dd, $J = 8.2, 1.6$ Hz, 1 H), 7.74 (s, 1 H), 7.57 (t, $J = 8.0$ Hz, 1 H), 7.47 (dd, $J = 8.2, 1.1$ Hz, 1 H), 7.43 (dd, $J = 8.2, 4.2$ Hz, 1 H), 7.20 (t, $J = 7.6$ Hz, 1 H),

7.00 (d, J = 7.1 Hz, 1 H), 4.90 (s, 3 H), 2.75 (s, 3 H); ^{13}C NMR (CDCl_3 , 100 MHz, ppm) δ 163.4, 148.2, 138.7, 136.4, 136.2, 135.5, 135.4, 128.1, 127.7, 126.9, 125.5, 122.1, 121.6, 120.8, 119.0, 116.3, 111.4, 37.8, 19.8; HRMS: calculated for $\text{C}_{20}\text{H}_{18}\text{N}_3\text{O}$ [M+H $^+$]: 316.1450; found: 316.1462.



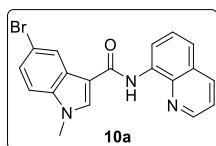
R_f = 0.50, 25 % EtOAc in hexanes

Prepared according to general procedure A. Purification of the crude product by flash column chromatography afforded the amide **8a** as white solid. ^1H NMR (CDCl_3 , 400 MHz, ppm): δ 10.46 (s, 1 H), 8.94-8.91 (m, 2 H), 8.20 (dd, J = 5.5, 1.6 Hz, 1 H), 8.18 (dd, J = 7.4, 2.1 Hz, 1 H), 7.94 (s, 1 H), 7.60 (t, J = 7.9 Hz, 1 H), 7.52 (dd, J = 8.2, 1.1 Hz, 1 H), 7.49 (dd, J = 8.3, 4.2 Hz, 1 H), 7.33 (dd, J = 8.9, 4.4 Hz, 1 H), 7.10 (td, J = 8.9, 2.4 Hz, 1 H), 3.91 (s, 3 H); ^{13}C NMR (CDCl_3 , 100 MHz, ppm) δ 163.0, 160.6, 158.2, 148.4, 138.7, 136.6, 135.3, 134.1, 134.0, 128.2, 127.7, 126.4, 126.2, 121.8, 121.1, 116.3, 111..9, 111.5, 111.2, 111.0, 110.9, 106.6, 106.4, 33.9; HRMS: calculated for $\text{C}_{19}\text{H}_{15}\text{FN}_3\text{O}$ [M+H $^+$]: 320.1199; found: 320.1205.



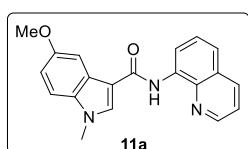
R_f = 0.50, 25 % EtOAc in hexanes

Prepared according to general procedure A. Purification of the crude product by flash column chromatography afforded the amide **9a** as white solid. ^1H NMR (CD_2Cl_2 , 400 MHz, ppm): δ 10.43 (s, 1 H), 8.93 (dd, J = 4.2, 1.6 Hz, 1 H), 8.87 (dd, J = 7.5, 1.4 Hz, 1 H), 8.48 (d, J = 1.8 Hz, 1 H), 8.26 (dd, J = 8.3, 1.5 Hz, 1 H), 7.97 (s, 1 H), 7.61 (t, J = 8.1 Hz, 1 H), 7.57-7.52 (m, 2 H), 7.38 (d, J = 8.8 Hz, 1 H), 7.31 (dd, J = 8.7, 1.9 Hz, 1 H), 3.89 (s, 3 H); ^{13}C NMR (CD_2Cl_2 , 100 MHz, ppm) δ 162.3, 160.5, 148.1, 138.2, 136.8, 135.9, 135.1, 133.5, 128.2, 127.6, 127.5, 126.9, 122.9, 121.7, 120.9, 120.5, 116.2, 111.3, 111.1, 33.6; HRMS: calculated for $\text{C}_{19}\text{H}_{15}\text{ClN}_3\text{O}$ [M+H $^+$]: 336.0904; found: 336.0909.



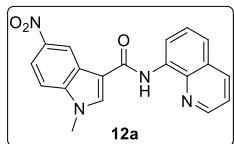
R_f = 0.50, 25 % EtOAc in hexanes

Prepared according to general procedure A. Purification of the crude product by flash column chromatography afforded the amide **10a** as white solid. ^1H NMR (CDCl_3 , 400 MHz, ppm): δ 10.49 (s, 1 H), 8.93-8.89 (m, 2 H), 8.72 (d, J = 1.6 Hz, 1 H), 8.19 (dd, J = 8.2, 1.4 Hz, 1 H), 7.88 (s, 1 H), 7.59 (t, J = 7.9 Hz, 1 H), 7.52 (dd, J = 7.2, 0.8 Hz, 1 H), 7.49 (dd, J = 8.3, 4.2 Hz, 1 H), 7.43 (dd, J = 8.7, 1.7 Hz, 1 H), 7.26 (t, J = 4.4 Hz, 1 H), 3.88 (s, 3 H); ^{13}C NMR (CDCl_3 , 100 MHz, ppm) δ 160.2, 151.7, 145.1, 141.4, 140.9, 138.7, 136.5, 136.1, 131.3, 130.0, 129.6, 129.0, 127.5, 126.9, 126.3, 125.2, 123.0, 122.1, 121.9, 117.9, 115.4, 114.3, 110.5, 107.6, 34.0; HRMS: calculated for $\text{C}_{19}\text{H}_{15}\text{BrN}_3\text{O}$ [M+H $^+$]: 380.0398; found: 380.0403.



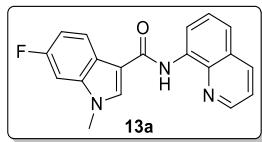
R_f = 0.50, 25 % EtOAc in hexanes

Prepared according to general procedure A. Purification of the crude product by flash column chromatography afforded the amide **11a** as white solid. **¹H NMR** (CDCl_3 , 400 MHz, ppm): δ 10.50 (s, 1 H), 8.97 (dd, J = 7.6, 0.9 Hz, 1 H), 8.84 (dd, J = 4.2, 1.6 Hz, 1 H), 8.19 (dd, J = 8.2, 1.6 Hz, 1 H), 7.99 (d, J = 2.3 Hz, 1 H), 7.87 (s, 1 H), 7.60 (t, J = 8.0 Hz, 1 H), 7.51 (dd, J = 8.2, 0.9 Hz, 1 H), 7.48 (dd, J = 8.4, 4.2 Hz, 1 H), 7.30 (d, J = 8.9 Hz, 1 H), 6.99 (dd, J = 8.9, 2.4 Hz, 1 H), 4.02 (s, 3 H), 3.88 (s, 3 H); **¹³C NMR** (CDCl_3 , 100 MHz, ppm) δ 163.5, 156.0, 148.1, 138.8, 136.6, 135.5, 133.1, 132.6, 128.2, 127.8, 126.2, 124.5, 121.7, 120.9, 116.3, 113.6, 111.4, 111.1, 102.0, 55.6, 33.8; **HRMS**: calculated for $\text{C}_{20}\text{H}_{18}\text{N}_3\text{O}_2$ [$\text{M}+\text{H}^+$]: 332.1399; **found**: 332.1403.



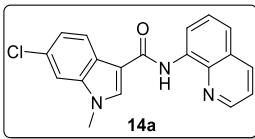
R_f = 0.50, 25 % EtOAc in hexanes

Prepared according to general procedure A. Purification of the crude product by flash column chromatography afforded the amide **12a** as yellow solid with a bad solubility. **¹H NMR** (CD_2Cl_2 , 400 MHz, ppm): δ 11.70 (s, 1 H), 10.60 (s, 1 H), 9.49 (s, 1 H), 8.98 (s, 1 H), 8.86 (dd, J = 19.3, 7.4 Hz, 1 H), 8.34-8.21 (m, 2 H), 7.65-7.48 (m, 4 H), 3.96 (s, 3 H); **¹³C NMR** (CDCl_3 , 100 MHz, ppm) δ 161.7, 158.1, 149.2, 148.8, 143.6, 140.2, 139.3, 138.8, 136.6, 136.3, 135.9, 134.9, 133.4, 128.2, 127.7, 127.2, 124.9, 123.3, 122.1, 122.0, 121.5, 118.5, 118.3, 117.3, 116.4, 114.5, 110.4, 34.1; **HRMS**: calculated for $\text{C}_{19}\text{H}_{15}\text{N}_4\text{O}_3$ [$\text{M}+\text{H}^+$]: 347.1144; **found**: 347.1142.



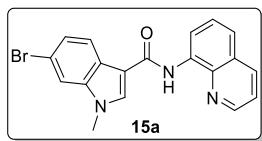
R_f = 0.50, 25 % EtOAc in hexanes

Prepared according to general procedure A. Purification of the crude product by flash column chromatography afforded the amide **13a** as white solid. **¹H NMR** (CDCl_3 , 400 MHz, ppm): δ 10.44 (s, 1 H), 8.92 (dd, J = 7.6, 1.2 Hz, 1 H), 8.86 (dd, J = 4.2, 1.6 Hz, 1 H), 8.38 (dd, J = 8.7, 2.5 Hz, 1 H), 8.17 (dd, J = 8.3, 1.6 Hz, 1 H), 7.85 (s, 1 H), 7.58 (t, J = 7.9 Hz, 1 H), 7.50 (dd, J = 8.2, 1.1 Hz, 1 H), 7.46 (dd, J = 8.2, 4.2 Hz, 1 H), 7.11(td, J = 9.2, 2.2 Hz, 1 H), 7.04 (dd, J = 9.3, 2.2 Hz, 1 H), 3.83 (s, 3 H); **¹³C NMR** (CDCl_3 , 100 MHz, ppm) δ 163.0, 161.4, 159.0, 148.3, 138.7, 137.7, 137.6, 136.5, 135.2, 132.9, 132.87, 128.2, 127.7, 122.4, 122.2, 122.1, 121.7, 121.0, 116.3, 112.1, 110.7, 110.5, 96.8, 96.5, 33.7; **HRMS**: calculated for $\text{C}_{19}\text{H}_{15}\text{FN}_3\text{O}$ [$\text{M}+\text{H}^+$]: 320.1199; **found**: 320.1210.



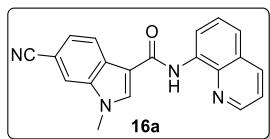
R_f = 0.50, 25 % EtOAc in hexanes

Prepared according to general procedure A. Purification of the crude product by flash column chromatography afforded the amide **14a** as white solid. **¹H NMR** (CDCl_3 , 400 MHz, ppm): δ 10.46 (s, 1 H), 8.92 (dd, J = 7.6, 1.2 Hz, 1 H), 8.87 (dd, J = 4.2, 1.6 Hz, 1 H), 8.37 (d, J = 8.6 Hz, 1 H), 8.18 (d, J = 8.2, 1.6 Hz, 1 H), 7.87 (s, 1 H), 7.59 (t, J = 7.9 Hz, 1 H), 7.51 (dd, J = 8.3, 1.2 Hz, 1 H), 7.48 (dd, J = 8.3, 1.2 Hz, 1 H), 7.38 (d, J = 1.7 Hz, 1 H), 7.33 (dd, J = 8.6, 1.8 Hz, 1 H), 3.86 (s, 3 H); **¹³C NMR** (CDCl_3 , 100 MHz, ppm) δ 162.9, 148.3, 138.7, 138.0, 136.6, 135.2, 133.2, 129.0, 128.2, 127.7, 124.4, 122.6, 122.0, 121.7, 121.1, 116.4, 112.2, 110.2, 33.7; **HRMS**: calculated for $\text{C}_{19}\text{H}_{15}\text{ClN}_3\text{O}$ [$\text{M}+\text{H}^+$]: 336.0904; **found**: 336.0914.



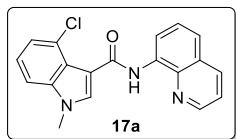
$R_f = 0.50$, 25 % EtOAc in hexanes

Prepared according to general procedure A. Purification of the crude product by flash column chromatography afforded the amide **15a** as white solid. **1H NMR** (CDCl_3 , 400 MHz, ppm): δ 10.45 (s, 1 H), 8.93-8.91 (m, 1 H), 8.87 (dd, $J = 4.2, 1.5$ Hz, 1 H), 8.32 (d, $J = 8.5$ Hz, 1 H), 8.18 (dd, $J = 8.2, 1.5$ Hz, 1 H), 7.85 (s, 1 H), 7.59 (t, $J = 7.9$ Hz, 1 H), 7.55-7.45 (m, 4 H), 3.85 (s, 3 H); **13C NMR** (CDCl_3 , 100 MHz, ppm) δ 162.8, 148.3, 138.7, 138.3, 136.5, 135.2, 133.1, 128.2, 127.7, 125.2, 124.7, 122.4, 121.7, 121.1, 116.6, 116.4, 113.3, 112.2, 33.7; **HRMS**: calculated for $\text{C}_{19}\text{H}_{15}\text{BrN}_3\text{O} [\text{M}+\text{H}^+]$: 380.0398; **found**: 380.0418.



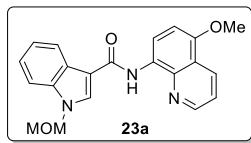
$R_f = 0.50$, 25 % EtOAc in hexanes

Prepared according to general procedure A. Purification of the crude product by flash column chromatography afforded the amide **16a** as white solid. **1H NMR** (CDCl_3 , 400 MHz, ppm): δ 10.48 (s, 1 H), 8.92-8.88 (m, 2 H), 8.21 (d, $J = 7.7$ Hz, 1 H), 8.07 (s, 1 H), 7.75 (s, 1 H), 7.63-7.49 (m, 4 H), 3.96 (s, 3 H); **13C NMR** (CDCl_3 , 100 MHz, ppm) δ 162.3, 148.4, 138.7, 136.7, 136.5, 135.6, 135.0, 129.0, 128.2, 127.7, 124.8, 122.1, 121.8, 121.4, 120.1, 116.5, 115.0, 112.9, 105.8, 33.9; **HRMS**: calculated for $\text{C}_{20}\text{H}_{15}\text{N}_4\text{O} [\text{M}+\text{H}^+]$: 327.1246; **found**: 327.1249.



$R_f = 0.50$, 25 % EtOAc in hexanes

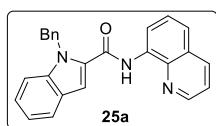
Prepared according to general procedure A. Purification of the crude product by flash column chromatography afforded the amide **17a** as white solid. **1H NMR** (CDCl_3 , 400 MHz, ppm): δ 10.43 (s, 1 H), 8.98 (dd, $J = 7.6, 1.0$ Hz, 1 H), 8.77 (dd, $J = 4.2, 1.6$ Hz, 1 H), 8.15 (dd, $J = 8.2, 1.6$ Hz, 1 H), 7.77 (s, 1 H), 7.59 (t, $J = 7.8$ Hz, 1 H), 7.51 (dd, $J = 8.2, 1.0$ Hz, 1 H), 7.42 (dd, $J = 8.2, 4.2$ Hz, 1 H), 7.30-7.20 (m, 3 H), 3.85 (s, 3 H); **13C NMR** (CDCl_3 , 100 MHz, ppm) δ 163.3, 148.2, 138.8, 138.6, 136.3, 135.3, 133.9, 128.2, 127.6, 126.4, 123.3, 122.9, 122.7, 121.6, 121.4, 116.7, 113.4, 108.7, 33.7; **HRMS**: calculated for $\text{C}_{19}\text{H}_{15}\text{ClN}_3\text{O} [\text{M}+\text{H}^+]$: 336.0904; **found**: 334.0908.



$R_f = 0.50$, 25 % EtOAc in hexanes

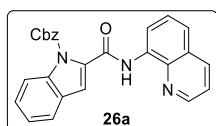
Prepared according to general procedure A. Purification of the crude product by flash column chromatography afforded the amide **22a** as white solid. **1H NMR** (CDCl_3 , 400 MHz, ppm): δ 10.35 (s, 1 H), 8.89 (dd, $J = 4.2, 1.6$ Hz, 1 H), 8.87 (d, $J = 8.5$ Hz, 1 H), 8.59 (dd, $J = 8.4, 1.6$ Hz, 1 H), 8.46 (d, $J = 7.5$ Hz, 1 H), 8.00 (s, 1 H), 7.58 (d, $J = 7.8$ Hz, 1 H), 7.46 (dd, $J = 8.4, 4.2$ Hz, 1 H), 7.43-7.34 (m, 2 H), 6.89 (d, $J = 8.6$ Hz, 1 H), 5.53 (s, 2 H), 4.00 (s, 3 H), 3.30 (s, 3 H); **13C NMR** (CDCl_3 , 100 MHz, ppm) δ 162.9, 150.1, 148.8,

139.4, 137.0, 132.1, 131.4, 128.7, 126.0, 123.3, 122.5, 120.9, 120.8, 120.6, 116.6, 113.5, 111.0, 104.6, 78.1, 56.3, 55.9; **HRMS**: calculated for C₂₁H₂₀N₃O₃ [M+H⁺]: 362.1505; **found**: 362.1507.



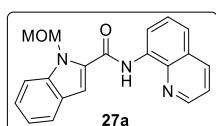
R_f = 0.50, 25 % EtOAc in hexanes

Prepared according to general procedure B. Purification of the crude product by flash column chromatography afforded the amide **24a** as white solid. **¹H NMR** (CDCl₃, 400 MHz, ppm): δ 10.76 (s, 1 H), 8.89 (dd, J = 4.2, 1.6 Hz, 1 H), 8.85 (dd, J = 6.8, 2.2 Hz, 1 H), 8.19 (dd, J = 8.2, 1.6 Hz, 1 H), 7.77 (d, J = 7.9 Hz, 1 H), 7.58-7.52 (m, 2 H), 7.50 (dd, J = 8.2, 4.2 Hz, 1 H), 7.40-7.37 (m, 2 H), 7.31-7.18 (m, 5 H), 7.17-7.15 (m, 2 H), 5.98 (s, 2 H); **¹³C NMR** (CDCl₃, 100 MHz, ppm) δ 160.6, 148.5, 139.3, 138.5, 136.5, 134.8, 132.2, 128.7, 128.2, 127.5, 127.2, 126.7, 126.5, 124.8, 122.3, 121.9, 121.7, 121.1, 116.5, 111.1, 106.0, 48.2; **HRMS**: calculated for C₂₅H₂₀N₃O [M+H⁺]: 378.1606; **found**: 368.1623.



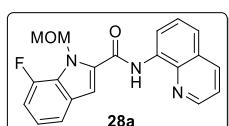
R_f = 0.50, 25 % EtOAc in hexanes

Prepared according to general procedure B. Purification of the crude product by flash column chromatography afforded the amide **25a** as white solid. **¹H NMR** (CDCl₃, 400 MHz, ppm): δ 10.29 (s, 1 H), 8.82 (dd, J = 5.9, 2.9 Hz, 1 H), 8.75 (dd, J = 4.2, 1.7 Hz, 1 H), 8.19-8.16 (m, 2 H), 7.62 (d, J = 7.7 Hz, 1 H), 7.57-7.55 (m, 2 H), 7.46-7.39 (m, 2 H), 7.32-7.28 (m, 3 H), 7.10-7.06 (m, 2 H), 7.04-7.00 (m, 2 H), 5.37 (s, 2 H); **¹³C NMR** (CDCl₃, 100 MHz, ppm) δ 160.4, 150.8, 148.4, 138.5, 137.2, 136.4, 134.9, 134.42, 134.37, 128.6, 128.5, 128.4, 128.2, 128.0, 127.5, 127.1, 126.7, 123.8, 122.2, 122.0, 121.8, 117.0, 115.5, 112.1, 69.7; **HRMS**: calculated for C₂₆H₂₀N₃O₃ [M+H⁺]: 422.1499; **found**: 422.1509.



R_f = 0.50, 25 % EtOAc in hexanes

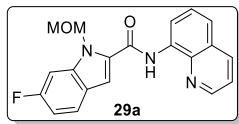
Prepared according to general procedure B. Purification of the crude product by flash column chromatography afforded the amide **26a** as white solid. **¹H NMR** (CDCl₃, 400 MHz, ppm): δ 10.74 (s, 1 H), 8.88-8.84 (m, 2 H), 8.14 (dd, J = 8.3, 1.6 Hz, 1 H), 7.74 (d, J = 7.7 Hz, 1 H), 7.60 (dd, J = 9.1, 0.7 Hz, 1 H), 7.55 (d, J = 7.6 Hz, 1 H), 7.51 (dd, J = 8.2, 1.4 Hz, 1 H), 7.45 (dd, J = 8.2, 4.2 Hz, 1 H), 7.40-7.36 (m, 1 H), 7.34 (s, 1 H), 7.23 (td, J = 6.0, 0.8 Hz, 1 H), 6.08 (s, 2 H), 3.36 (s, 3 H); **¹³C NMR** (CDCl₃, 100 MHz, ppm) δ 160.3, 148.5, 139.5, 138.6, 136.4, 134.6, 132.3, 128.1, 127.4, 126.6, 125.2, 122.3, 121.84, 121.82, 121.6, 116.5, 111.3, 107.2, 74.9, 56.2; **HRMS**: calculated for C₂₀H₁₈N₃NaO [M+Na⁺]: 354.1213; **found**: 354.1217.



R_f = 0.50, 25 % EtOAc in hexanes

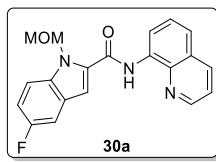
Prepared according to general procedure B. Purification of the crude product by flash column

chromatography afforded the amide **27a** as white solid. **¹H NMR** (CDCl_3 , 400 MHz, ppm): δ 10.76 (s, 1 H), 8.90-8.87 (m, 2 H), 8.2 (dd, J = 8.2, 1.2 Hz, 1 H), 7.61-7.55 (m, 2 H), 7.51-7.48 (m, 2 H), 7.35 (d, J = 1.5 Hz, 1 H), 7.15-7.04 (m, 2 H), 6.20 (s, 2 H), 3.35 (s, 3 H); **¹³C NMR** (CDCl_3 , 100 MHz, ppm) δ 160.0, 151.7, 149.2, 148.5, 138.7, 136.6, 134.6, 133.9, 130.3, 130.3, 128.2, 127.5, 127.3, 125.2, 122.1, 121.9, 121.7, 121.6, 118.14, 118.11, 116.8, 111.0, 110.9, 108.2, 56.1; **HRMS**: calculated for $\text{C}_{20}\text{H}_{16}\text{FN}_3\text{NaO}_2$ [$\text{M}+\text{Na}^+$]: 372.1124; **found**: 372.1137.



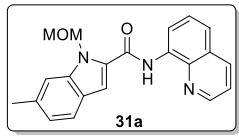
R_f = 0.50, 25 % EtOAc in hexanes

Prepared according to general procedure B. Purification of the crude product by flash column chromatography afforded the amide **28a** as white solid. **¹H NMR** (CDCl_3 , 400 MHz, ppm): δ 10.72 (s, 1 H), 8.89-8.85 (m, 2 H), 8.21 (dd, J = 8.3, 1.6 Hz, 1 H), 7.68 (dd, J = 8.7, 5.4 Hz, 1 H), 7.60 (t, J = 7.5 Hz, 1 H), 7.56 (dd, J = 8.3, 1.8 Hz, 1 H), 7.51 (dd, J = 8.2, 4.2 Hz, 1 H), 7.34 (s, 1 H), 7.28 (dd, J = 9.8, 2.2 Hz, 1 H), 7.00 (td, J = 9.2, 2.3 Hz, 1 H), 6.04 (s, 2 H), 3.37 (s, 3 H); **¹³C NMR** (CDCl_3 , 100 MHz, ppm) δ 162.9, 160.1, 148.5, 139.9, 138.7, 136.6, 134.6, 133.1, 128.2, 127.5, 123.5, 123.4, 123.1, 121.9, 116.6, 111.2, 110.9, 107.3, 97.9, 97.7, 75.3, 56.3; **HRMS**: calculated for $\text{C}_{20}\text{H}_{16}\text{FN}_3\text{NaO}_2$ [$\text{M}+\text{Na}^+$]: 372.1124; **found**: 372.1135.



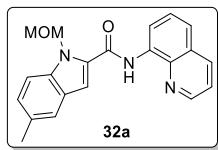
R_f = 0.50, 25 % EtOAc in hexanes

Prepared according to general procedure B. Purification of the crude product by flash column chromatography afforded the amide **29a** as white solid. **¹H NMR** (CDCl_3 , 400 MHz, ppm): δ 10.75 (s, 1 H), 8.89-8.86 (m, 2 H), 8.20 (dd, J = 8.3, 1.6 Hz, 1 H), 7.62-7.53 (m, 3 H), 7.50 (dd, J = 8.2, 4.2 Hz, 1 H), 7.38 (dd, J = 9.0, 2.5 Hz, 1 H), 7.30 (s, 1 H), 7.14 (td, J = 9.1, 2.5 Hz, 1 H), 6.07 (s, 2 H), 3.36 (s, 3 H); **¹³C NMR** (CDCl_3 , 100 MHz, ppm) δ 160.1, 160.0, 157.6, 148.6, 138.7, 136.6, 136.1, 134.6, 133.9, 128.2, 127.5, 127.0, 126.9, 122.1, 122.0, 116.6, 114.2, 113.9, 112.5, 112.4, 106.84, 106.80, 106.6, 75.2, 56.2; **HRMS**: calculated for $\text{C}_{20}\text{H}_{16}\text{FN}_3\text{NaO}_2$ [$\text{M}+\text{Na}^+$]: 372.1124; **found**: 372.1130.



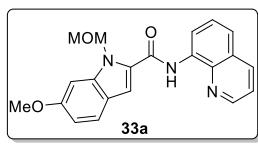
R_f = 0.50, 25 % EtOAc in hexanes

Prepared according to general procedure B. Purification of the crude product by flash column chromatography afforded the amide **30a** as white solid. **¹H NMR** (CDCl_3 , 400 MHz, ppm): δ 10.73 (s, 1 H), 8.89-8.96 (m, 2 H), 8.19 (dd, J = 8.2, 1.4 Hz, 1 H), 7.63 (d, J = 8.1 Hz, 1 H), 7.59 (t, J = 7.8 Hz, 1 H), 7.54 (dd, J = 8.2, 1.3 Hz, 1 H), 7.49 (dd, J = 8.2, 4.2 Hz, 1 H), 7.40 (s, 1 H), 7.32 (s, 1 H), 7.07 (d, J = 8.1 Hz, 1 H), 6.07 (s, 2 H), 3.38 (s, 3 H), 2.53 (s, 3 H); **¹³C NMR** (CDCl_3 , 100 MHz, ppm) δ 160.5, 148.5, 140.1, 138.7, 136.5, 135.5, 134.8, 131.8, 128.2, 127.5, 124.5, 123.7, 121.91, 121.89, 121.8, 116.5, 111.1, 107.3, 74.9, 56.2, 22.3; **HRMS**: calculated for $\text{C}_{21}\text{H}_{19}\text{N}_3\text{NaO}_2$ [$\text{M}+\text{Na}^+$]: 368.1375; **found**: 368.1378.



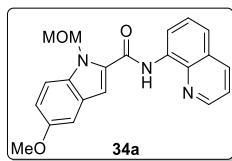
$R_f = 0.50$, 25 % EtOAc in hexanes

Prepared according to general procedure B. Purification of the crude product by flash column chromatography afforded the amide **31a** as white solid. **¹H NMR** (CDCl_3 , 400 MHz, ppm): δ 10.74 (s, 1 H), 8.88-8.86 (m, 2 H), 8.18 (dd, $J = 8.2, 1.6$ Hz, 1 H), 7.58 (t, $J = 7.8$ Hz, 1 H), 7.55-7.47 (m, 4 H), 7.26 (d, $J = 9.3$ Hz, 1 H), 7.21 (dd, $J = 8.5, 1.3$ Hz, 1 H), 6.07 (s, 2 H), 3.35 (s, 3 H), 2.48 (s, 3 H); **¹³C NMR** (CDCl_3 , 100 MHz, ppm) δ 160.5, 148.5, 138.7, 138.1, 136.5, 134.8, 132.4, 131.0, 128.2, 127.5, 127.1, 126.9, 121.9, 121.8, 121.7, 116.5, 111.0, 106.8, 75.0, 56.1, 21.6; **HRMS**: calculated for $\text{C}_{21}\text{H}_{19}\text{N}_3\text{NaO}_2$ [$\text{M}+\text{Na}^+$]: 368.1375; **found**: 368.1383.



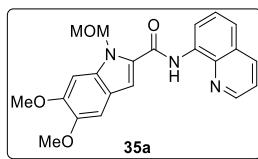
$R_f = 0.50$, 25 % EtOAc in hexanes

Prepared according to general procedure B. Purification of the crude product by flash column chromatography afforded the amide **32a** as white solid. **¹H NMR** (CDCl_3 , 400 MHz, ppm): δ 10.69 (s, 1 H), 8.88-8.84 (m, 2 H), 8.18 (dd, $J = 8.2, 1.6$ Hz, 1 H), 7.61 (d, $J = 8.7$ Hz, 1 H), 7.57 (d, $J = 7.6$ Hz, 1 H), 7.53 (dd, $J = 8.2, 1.4$ Hz, 1 H), 7.48 (dd, $J = 8.2, 4.2$, 1 H), 7.30 (s, 1 H), 7.02 (d, $J = 2.0$ Hz, 1 H), 6.90 (dd, $J = 8.7, 2.2$ Hz, 1 H), 6.07 (s, 2 H), 3.91 (s, 3 H), 3.38 (s, 3 H); **¹³C NMR** (CDCl_3 , 100 MHz, ppm) δ 160.4, 158.8, 148.4, 140.8, 138.7, 136.5, 134.8, 131.3, 128.2, 127.5, 123.0, 121.9, 121.6, 120.7, 116.4, 112.8, 107.6, 93.7, 75.0, 56.1, 55.7; **HRMS**: calculated for $\text{C}_{21}\text{H}_{19}\text{N}_3\text{NaO}_3$ [$\text{M}+\text{Na}^+$]: 384.1324; **found**: 384.1325.



$R_f = 0.50$, 25 % EtOAc in hexanes

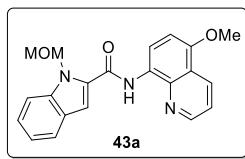
Prepared according to general procedure B. Purification of the crude product by flash column chromatography afforded the amide **33a** as white solid. **¹H NMR** (CDCl_3 , 400 MHz, ppm): δ 10.74 (s, 1 H), 8.89-8.86 (m, 2 H), 8.20 (dd, $J = 8.3, 1.6$ Hz, 1 H), 7.59 (t, $J = 7.8$ Hz, 1 H), 7.55 (dd, $J = 8.3, 1.6$ Hz, 1 H), 7.52-7.48 (m, 2 H), 7.29 (s, 1 H), 7.17 (d, $J = 2.4$ Hz, 1 H), 7.06 (dd, $J = 9.0, 2.5$ Hz, 1 H), 6.06 (s, 2 H), 3.89 (s, 3 H), 3.36 (s, 3 H); **¹³C NMR** (CDCl_3 , 100 MHz, ppm) δ 160.4, 155.4, 148.5, 138.7, 136.5, 134.9, 134.7, 132.7, 128.2, 127.6, 127.0, 121.9, 121.8, 116.5, 116.3, 112.3, 106.8, 102.7, 75.1, 56.1, 55.9; **HRMS**: calculated for $\text{C}_{21}\text{H}_{19}\text{N}_3\text{NaO}_3$ [$\text{M}+\text{Na}^+$]: 384.1324; **found**: 384.1339.



$R_f = 0.50$, 25 % EtOAc in hexanes

Prepared according to general procedure B. Purification of the crude product by flash column chromatography afforded the amide **34a** as white solid. **¹H NMR** (CDCl_3 , 400 MHz, ppm): δ 10.68 (s, 1 H),

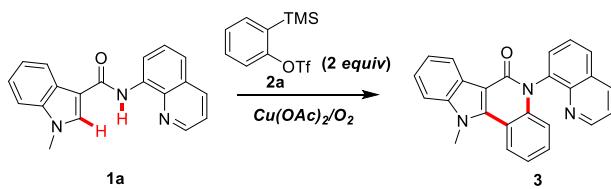
8.88-8.84 (m, 2 H), 8.19 (dd, J = 8.3, 1.7 Hz, 1 H), 7.59 (t, J = 7.8 Hz, 1 H), 7.53 (dd, J = 8.3, 1.4 Hz, 1 H), 7.49 (dd, J = 8.3, 4.2 Hz, 1 H), 7.28 (s, 1 H), 7.14 (s, 1 H), 7.03 (s, 1 H), 6.08 (s, 2 H), 4.00 (s, 3 H), 3.96 (s, 3 H), 3.38 (s, 3 H); ^{13}C NMR (CDCl_3 , 100 MHz, ppm) δ 160.4, 149.8, 148.4, 146.7, 138.7, 136.5, 134.9, 134.7, 130.8, 128.2, 127.6, 121.9, 121.6, 119.4, 116.4, 107.3, 102.5, 93.8, 75.2, 56.35, 56.34, 56.0; HRMS: calculated for $\text{C}_{22}\text{H}_{21}\text{N}_3\text{NaO}_4$ [M+Na $^+$]: 414.1430; found: 414.1444.



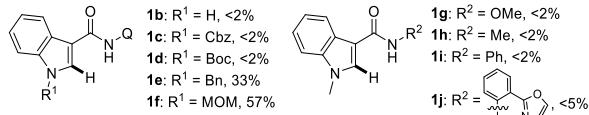
$R_f = 0.50$, 25 % EtOAc in hexanes

Prepared according to general procedure B. Purification of the crude product by flash column chromatography afforded the amide **43a** as white solid. **¹H NMR** (CDCl_3 , 400 MHz, ppm): δ 10.52 (s, 1 H), 8.89 (dd, J = 4.2, 1.7 Hz, 1 H), 8.61 (dd, J = 8.4, 1.7 Hz, 1 H), 7.75 (d, J = 7.9 Hz, 1 H), 7.61 (d, J = 8.4 Hz, 1 H), 7.48 (dd, J = 8.4, 4.2 Hz, 1 H), 7.40-7.36 (m, 1 H), 7.32 (s, 1 H), 7.25-7.21 (m, 1 H), 6.89 (d, J = 8.6 Hz, 1 H), 6.09 (s, 2 H), 4.02 (s, 3 H), 3.37 (s, 3 H); **¹³C NMR** (CDCl_3 , 100 MHz, ppm) δ 160.1, 150.7, 149.0, 139.5, 132.8, 131.5, 128.1, 126.7, 125.0, 122.2, 121.6, 121.0, 120.7, 116.8, 111.3, 106.9, 104.5, 75.0, 56.2, 56.0; **HRMS**: calculated for $\text{C}_{21}\text{H}_{20}\text{N}_3\text{O}_3$ [$\text{M}+\text{H}^+$]: 362.1499; **found**: 362.1504.

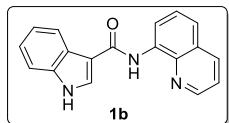
3. Cu-mediated annulation of C(sp²)-H/N-H bonds with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate.^a



Entry ^a	reagents (equiv)	solvents	yield 3 (%) ^b
1	Cu(OAc) ₂ (0.35), CsF (1.2), TBAI (0.5), O ₂ , 80 °C	DMF	10
2	Cu(OAc) ₂ (0.35), CsF (1.2), TBAI (0.5), O ₂ , 80 °C	MeCN	12
3	Cu(OAc) ₂ (0.35), CsF (1.2), TBAI (0.5), O ₂ , 80 °C	DMF:MeCN(1:1)	21
4	Cu(OAc) ₂ (0.35), NaF (1.2), TBAI (0.5), O ₂ , 80 °C	DMF:MeCN(1:1)	<2
5	Cu(OAc) ₂ (0.35), KF (1.2), TBAI (0.5), O ₂ , 80 °C	DMF:MeCN(1:1)	18
6	Cu(OAc) ₂ (0.35), CsF (1.2), TBAB (0.5), O ₂ , 80 °C	DMF:MeCN(1:1)	20
7	Cu(OAc) ₂ (0.35), CsF (2.4), TBAI (0.5), O ₂ , 80 °C	DMF:MeCN(1:1)	23
8	Cu(OAc) ₂ (0.35), CsF (1.2), TBAI (1.0), O ₂ , 80 °C	DMF:MeCN(1:1)	31
9	Cu(OAc) ₂ (0.5), CsF (1.2), TBAI (0.5), O ₂ , 80 °C	DMF:MeCN(1:1)	43
10	Cu(OAc) ₂ (1.0), CsF (1.2), TBAI (0.5), O ₂ , 80 °C	DMF:MeCN(1:1)	12
11	Cu(OAc) ₂ (0.5), CsF (1.2), TBAI (1.0), O ₂ , 80 °C	DMF:MeCN(1:1)	78(81) ^c
12	Cu(OAc) ₂ (0.5), CsF (1.2), TBAI (1.0), O ₂ , 40 °C	DMF:MeCN(1:1)	19
13	Cu(OAc) ₂ (0.5), CsF (1.2), TBAI (1.0), O ₂ , 100 °C	DMF:MeCN(1:1)	55

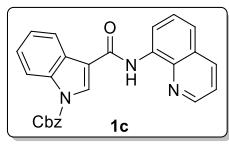


^aAll screening reactions were carried out in a 10 mL glass vial with a PTEE-lined cap on a 0.2 mmol scale. ^bYields are based on ¹H NMR analysis of the reaction mixture use 1,2-dichloroethane as an internal standard. ^cIsolated yield in parentheses. DMF = *N,N*-dimethylformamide, TBAB = tetra-*n*-butylammonium bromide, TBAI = tetra-*n*-butylammonium iodide.



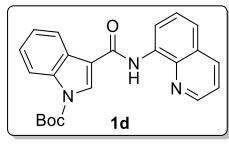
$R_f = 0.50$, 50 % EtOAc in hexanes

Prepared according to general procedure A. Purification of the crude product by flash column chromatography afforded the amide **1b** as white solid. **¹H NMR** (DMSO, 400 MHz, ppm): δ 11.96 (s, 1 H), 10.40 (s, 1 H), 9.00 (dd, J = 4.1, 1.4 Hz, 1 H), 8.80 (dd, J = 7.0, 1.7 Hz, 1 H), 8.44 (dd, J = 8.2, 1.4 Hz, 1 H), 8.32-8.29 (m, 2 H), 7.68-7.55 (m, 4 H), 7.30-7.25 (m, 2 H); **¹³C NMR** (DMSO, 100 MHz, ppm) δ 162.7, 148.9, 137.9, 136.7, 136.6, 134.8, 129.7, 127.8, 127.2, 124.9, 122.3, 122.2, 121.2, 121.1, 119.9, 115.8, 112.6, 111.0; **HRMS**: calculated for $C_{18}H_{15}N_3O$ [M+H⁺]: 288.1137; **found**: 288.1157.



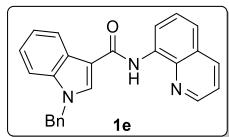
$R_f = 0.50$, 25 % EtOAc in hexanes

Prepared according to general procedure A. Purification of the crude product by flash column chromatography afforded the amide **1c** as white solid. **¹H NMR** (CDCl₃, 400 MHz, ppm): δ 10.57 (s, 1 H), 8.92 (dd, J = 7.5, 1.3 Hz, 1 H), 8.87 (dd, J = 4.2, 1.6 Hz, 1 H), 8.42 (s, 1 H), 8.41-8.39 (m, 1 H), 8.27 (d, J = 6.6 Hz, 1 H), 8.19 (dd, J = 8.2, 1.6 Hz, 1 H), 7.59 (t, J = 7.9 Hz, 1 H), 7.55-7.52 (m, 3 H), 7.50-7.41 (m, 6 H), 5.53 (s, 2 H); **¹³C NMR** (CDCl₃, 100 MHz, ppm) δ 162.1, 150.7, 148.5, 138.7, 136.5, 135.9, 134.8, 134.7, 129.1, 129.0, 128.8, 128.7, 128.1, 127.6, 127.3, 125.7, 124.5, 121.8, 121.7, 121.3, 118.1, 116.2, 115.6, 69.6; **HRMS**: calculated for $C_{26}H_{20}N_3O_3$ [M+H⁺]: 422.1505; **found**: 422.1517.



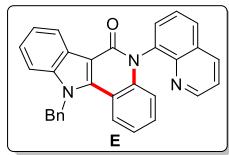
$R_f = 0.50$, 25 % EtOAc in hexanes

Prepared according to general procedure A. Purification of the crude product by flash column chromatography afforded the amide **1d** as white solid. **¹H NMR** (CDCl₃, 400 MHz, ppm): δ 10.58 (s, 1 H), 8.93 (d, J = 7.0 Hz, 1 H), 8.86 (dd, J = 4.2, 1.4 Hz, 1 H), 8.43-8.40 (m, 2 H), 8.24-8.22 (m, 1 H), 8.16 (dd, J = 8.2, 1.4 Hz, 1 H), 7.59 (t, J = 7.9 Hz, 1 H), 7.52 (d, J = 7.5 Hz, 1 H), 7.48-7.40 (m, 3 H), 1.72 (s, 9 H); **¹³C NMR** (CDCl₃, 100 MHz, ppm) δ 162.3, 149.4, 148.4, 138.7, 136.5, 135.8, 134.8, 129.1, 128.1, 127.6, 127.3, 125.3, 124.1, 121.8, 121.6, 121.2, 117.1, 116.6, 115.6, 85.2, 28.2; **HRMS**: calculated for $C_{23}H_{22}N_3O_3$ [M+H⁺]: 388.1661; **found**: 388.1666.



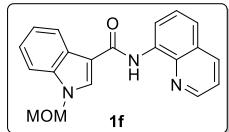
$R_f = 0.50$, 25 % EtOAc in hexanes

Prepared according to general procedure A. Purification of the crude product by flash column chromatography afforded the amide **1f** as white solid. **¹H NMR** (CDCl_3 , 400 MHz, ppm): δ 10.59 (dd, $J = 7.6, 1.2$ Hz, 1 H), 8.96 (dd, $J = 7.6, 1.2$ Hz, 1 H), 8.89 (dd, $J = 4.2, 1.6$ Hz, 1 H), 8.50 (d, $J = 7.9$ Hz, 1 H), 8.19 (dd, $J = 8.2, 1.6$ Hz, 1 H), 8.01 (s, 1 H), 7.60 (t, $J = 8.0$ Hz, 1 H), 7.51 (dd, $J = 8.2, 1.2$ Hz, 1 H), 7.48 (dd, $J = 8.2, 4.2$ Hz, 1 H), 7.40-7.27 (m, 6 H), 7.20-7.18 (m, 2 H), 5.42 (s, 2 H); **¹³C NMR** (CDCl_3 , 100 MHz, ppm) δ 163.4, 148.3, 138.8, 137.2, 136.5, 136.2, 135.5, 132.8, 129.1, 128.22, 128.19, 127.8, 127.1, 125.8, 123.0, 122.2, 121.7, 121.0, 120.9, 116.5, 112.6, 110.8, 50.9; **HRMS**: calculated for $\text{C}_{25}\text{H}_{20}\text{N}_3\text{O} [\text{M}+\text{H}^+]$: 378.1606; **found**: 378.1613.



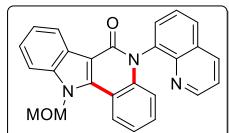
$R_f = 0.50$, 50 % EtOAc in hexanes

Prepared according to general procedure I . Purification of the crude product by flash column chromatography afforded the annulation product **F** as white solid in 33% yield (30 mg). **¹H NMR** (CDCl_3 , 400 MHz, ppm): δ 8.80 (dd, $J = 4.2, 1.6$ Hz, 1 H), 8.57 (d, $J = 7.5$ Hz, 1 H), 8.29 (dd, $J = 8.3, 1.6$ Hz, 1 H), 8.05 (dd, $J = 7.9, 1.6$ Hz, 1 H), 8.02 (d, $J = 8.3$ Hz, 1 H), 7.82 (dd, $J = 7.2, 1.6$ Hz, 1 H), 7.78 (t, $J = 7.7$ Hz, 1 H), 7.46-7.37 (m, 6 H), 7.34 (d, $J = 7.1$ Hz, 1 H), 7.31-7.29 (m, 2 H), 7.19-7.15 (m, 1 H), 7.09-7.06 (m, 1 H), 6.64 (d, $J = 8.4$ Hz, 1 H), 5.97 (s, 2 H); **¹³C NMR** (CDCl_3 , 100 MHz, ppm) δ 160.5, 151.6, 145.2, 141.2, 140.4, 140.3, 136.51, 136.48, 136.3, 131.3, 130.0, 129.5, 129.4, 128.6, 128.0, 127.0, 126.1, 125.02, 124.98, 123.0, 122.7, 122.5, 122.0, 121.9, 117.7, 113.8, 109.3, 108.9, 49.6; **HRMS**: calculated for $\text{C}_{31}\text{H}_{22}\text{N}_3\text{O} [\text{M}+\text{H}^+]$: 452.1763; **found**: 452.1770.



$R_f = 0.50$, 25 % EtOAc in hexanes

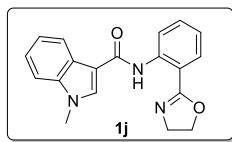
Prepared according to general procedure A. Purification of the crude product by flash column chromatography afforded the amide **1e** as white solid. **¹H NMR** (CDCl_3 , 400 MHz, ppm): δ 10.56 (s, 1 H), 8.95 (dd, $J = 7.6, 1.2$ Hz, 1 H), 8.86 (dd, $J = 4.2, 1.3$ Hz, 1 H), 8.47 (d, $J = 7.7$ Hz, 1 H), 8.14 (d, $J = 8.2$ Hz, 1 H), 8.00 (s, 1 H), 7.59-7.55 (m, 2 H), 7.48 (d, $J = 8.1$ Hz, 1 H), 7.45-7.33 (m, 3 H), 5.50 (s, 2 H), 3.28 (s, 3 H); **¹³C NMR** (CDCl_3 , 100 MHz, ppm) δ 163.1, 148.3, 138.7, 136.9, 136.4, 135.2, 132.2, 128.1, 127.6, 126.0, 123.4, 122.6, 121.7, 121.1, 120.9, 116.4, 113.3, 111.0, 78.1, 56.3; **HRMS**: calculated for $\text{C}_{20}\text{H}_{18}\text{N}_3\text{O}_2 [\text{M}+\text{H}^+]$: 332.1399; **found**: 332.1408.



$R_f = 0.50$, 50 % EtOAc in hexanes

Prepared according to general procedure I . Purification of the crude product by flash column chromatography afforded the annulation product **E** as white solid in 57% yield (46.3 mg). **¹H NMR** (CDCl_3 , 400 MHz, ppm): δ 8.79 (dd, $J = 4.2, 1.6$ Hz, 1 H), 8.54-8.50 (m, 2 H), 8.28 (dd, $J = 8.4, 1.7$ Hz, 1 H), 8.05 (dd, $J = 7.9, 1.7$ Hz, 1

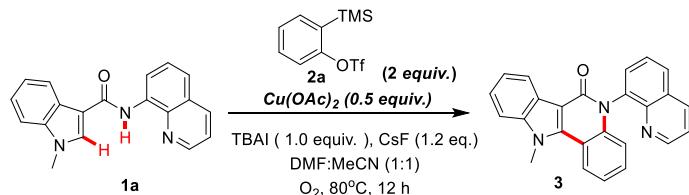
H), 7.81 (dd, J = 7.1, 1.7 Hz, 1 H), 7.77 (t, J = 7.5 Hz, 1 H), 7.64 (d, J = 8.3 Hz, 1 H), 7.47-7.40 (m, 2 H), 7.35 (t, J = 7.6 Hz, 1 H), 7.31-7.22 (m, 2 H), 6.65 (dd, J = 8.2, 1.0 Hz, 1 H), 5.95 (dd, J = 13.2, 12.2 Hz, 2 H), 3.56 (s, 3 H); ^{13}C NMR (CDCl_3 , 100 MHz, ppm) δ 160.4, 151.6, 145.1, 141.2, 140.9, 140.5, 136.5, 136.2, 131.3, 130.0, 129.5, 128.9, 127.0, 125.1, 125.0, 124.2, 122.8, 122.6, 122.2, 122.0, 117.5, 113.8, 109.7, 109.0, 75.6, 56.5; HRMS: calculated for $\text{C}_{26}\text{H}_{20}\text{N}_3\text{O}_2$ [M+H $^+$]: 406.1556; found: 406.1553.



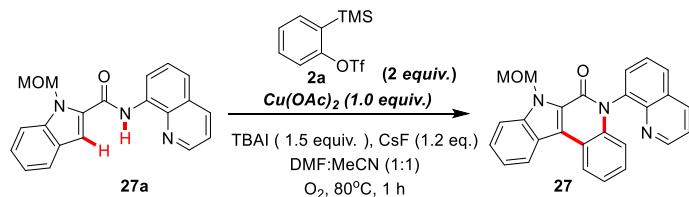
R_f = 0.50, 25 % EtOAc in hexanes

Prepared according to general procedure A. Purification of the crude product by flash column chromatography afforded the amide **1g** as white solid. ^1H NMR (CDCl_3 , 400 MHz, ppm): δ 12.59 (s, 1 H), 8.97-8.95 (m, 1 H), 8.47-8.43 (m, 1 H), 7.87 (dd, J = 7.9, 1.6 Hz, 1 H), 7.78 (s, 1 H), 7.52-7.48 (m, 1 H), 7.35-7.26 (m, 3 H), 7.07-7.03 (m, 1 H), 4.42-4.37 (m, 2 H), 4.20-4.15 (m, 2 H), 3.83 (s, 3 H); ^{13}C NMR (CDCl_3 , 100 MHz, ppm) δ 165.1, 164.0, 141.0, 137.4, 132.7, 132.2, 129.4, 126.7, 122.9, 122.0, 121.6, 119.9, 112.9, 112.1, 109.7, 66.2, 54.8, 33.6; HRMS: calculated for $\text{C}_{19}\text{H}_{18}\text{N}_3\text{O}_2$ [M+H $^+$]: 320.1399; found: 320.1407.

4. General procedures for Cu-mediated C(sp²)-H/N-H Annulation reactions with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate.

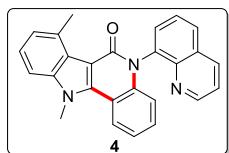


General procedure I : A mixture of amide **1a** (60 mg, 0.2 mmol, 1 equiv.), $\text{Cu}(\text{OAc})_2$ (18.2 mg, 0.1 mmol, 0.5 equiv.), TBAI (74 mg, 0.2 mmol, 1.0 equiv.), CsF (36.5 mg, 0.24 mmol, 1.2 equiv.), and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (120 mg, 2 equiv.) in DMF (1.0 mL)/MeCN (1.0 mL) in a 10 mL glass vial (purged with O_2 , sealed with PTFE cap) was heated at 80°C for 12 hours. The reaction mixture was cooled to RT. The resulting residue was purified by silica gel flash chromatography to give the annulation product **3** in 81% (62 mg) isolated yield (R_f = 0.4, 50% EtOAc in hexanes). ^1H NMR (DMSO, 400 MHz, ppm): δ 8.70 (d, J = 2.6 Hz, 1 H), 8.65-8.63 (m, 1 H), 8.56 (d, J = 7.3 Hz, 1 H), 8.26-8.21 (m, 2 H), 7.89-7.85 (m, 3 H), 7.59 (dd, J = 8.2, 4.1 Hz, 1 H), 7.47 (t, J = 7.2 Hz, 1 H), 7.35-7.29 (m, 3 H), 6.52-6.50 (m, 1 H), 4.43 (s, 3 H); ^{13}C NMR (DMSO, 100 MHz, ppm) δ 151.2, 144.3, 140.8, 139.7, 136.7, 135.8, 131.4, 129.5, 129.0, 127.0, 124.4, 123.7, 123.6, 122.2, 121.7, 120.8, 117.0, 113.5, 110.5, 106.7, 33.7; HRMS: calculated for $\text{C}_{25}\text{H}_{18}\text{N}_3\text{O}$ [M+H $^+$]: 376.1444; found: 376.1460. **1 gram scale reaction:** A mixture of amide **1a** (900 mg, 3.0 mmol, 1 equiv.), $\text{Cu}(\text{OAc})_2$ (272 mg, 1.5 mmol, 0.5 equiv.), TBAI (1.1 g, 3.0 mmol, 1.0 equiv.) and CsF (548 mg, 3.6 mmol, 1.2 equiv.) in DMF (15.0 mL)/MeCN (15.0 mL) in a 100 mL flask purged with O_2 and heated at 80°C for 30 min. And then 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (1.8 mL, 6 mmol, 2 equiv.) was added under constant oxygen with a stainless steel needle. The mixture was cooled to RT after reacting for 12 hours under 80°C. The resulting residue was purified by silica gel flash chromatography to give the annulation product **3** in 65% isolated yield as with the solid.



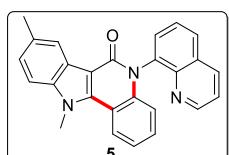
General procedure II: A mixture of amide **1a** (60 mg, 0.2 mmol, 1 equiv.), Cu(OAc)₂ (27 mg, 0.15 mmol, 0.75 equiv.), TBAI (111 mg, 0.3 mmol, 1.5 equiv.), CsF (36.5 mg, 1.2 equiv.), and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (120 mg, 2 equiv.) in DMF (1.0 mL)/MeCN (1.0 mL) in a 10 mL glass vial (purged with O₂, sealed with PTFE cap) was heated at 100 °C for 0.5 hour. The reaction mixture was cooled to RT. The resulting residue was purified by silica gel flash chromatography to give the annulation product **27** in 65% (53 mg) isolated yield ($R_f = 0.4$, 50% EtOAc in hexanes). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 8.77 (dd, $J = 4.2$, 1.7 Hz, 1 H), 8.58 (dd, $J = 8.1$, 1.1 Hz, 1 H), 8.51 (d, $J = 8.1$ Hz, 1 H), 8.27 (dd, $J = 8.3$, 1.6 Hz, 1 H), 8.05 (dd, $J = 8.1$, 1.6 Hz, 1 H), 7.82 (dd, $J = 7.3$, 1.6 Hz, 1 H), 7.77 (t, $J = 7.6$ Hz, 2 H), 7.57 (td, $J = 7.2$, 0.8 Hz, 1 H), 7.45-7.40 (m, 2 H), 7.36-7.32 (m, 1 H), 7.18-7.14 (m, 1 H), 6.58 (dd, $J = 8.6$, 0.6 Hz, 1 H), 6.42 (d, $J = 10.4$ Hz, 1 H), 6.23 (d, $J = 10.4$ Hz, 1 H), 3.35 (s, 3 H); ¹³C NMR (CDCl₃, 100 MHz, ppm) δ 157.0, 151.6, 144.8, 140.9, 138.2, 136.5, 136.1, 131.0, 129.9, 129.6, 126.9, 126.8, 126.5, 126.4, 123.9, 123.0, 122.9, 122.8, 122.1, 122.1, 121.3, 119.3, 116.9, 112.1, 55.9; HRMS: calculated for C₂₆H₁₉N₃NaO₂ [M+Na⁺]: 428.1375; found: 428.1372.

5. Substrate scope of the Cu-mediated C-H/N-H annulation reactions.



$R_f = 0.50$, 50 % EtOAc in hexanes

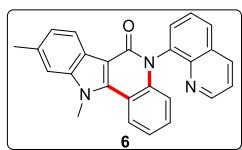
Prepared according to general procedure I . Purification of the crude product by flash column chromatography afforded the annulation product **4** as white solid in 42% yield (33 mg). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 8.79 (dd, $J = 4.2$, 1.7 Hz, 1 H), 8.42 (dd, $J = 8.1$, 1.6 Hz, 1 H), 8.27 (dd, $J = 8.3$, 1.7 Hz, 1 H), 8.02 (dd, $J = 8.0$, 1.6 Hz, 1 H), 7.81 (dd, $J = 7.2$, 1.7 Hz, 1 H), 7.76 (t, $J = 7.9$ Hz, 1 H), 7.41 (dd, $J = 8.3$, 4.2 Hz, 1 H), 7.36-7.30 (m, 2 H), 7.24-7.16 (m, 2 H), 7.09-7.08 (m, 1 H), 6.52 (dd, $J = 8.1$, 1.7 Hz, 1 H), 4.33 (s, 3 H), 3.09 (s, 3 H); ¹³C NMR (CDCl₃, 100 MHz, ppm) δ 160.1, 151.5, 145.1, 141.3, 141.0, 140.9, 137.1, 136.5, 134.6, 131.3, 130.1, 129.3, 128.4, 127.1, 124.7, 124.5, 124.2, 123.2, 122.0, 121.3, 117.4, 114.1, 109.5, 106.8, 34.4, 24.1; HRMS: calculated for C₂₆H₂₀N₃O [M+H⁺]: 390.1606; found: 390.1598.



$R_f = 0.55$, 50 % EtOAc in hexanes

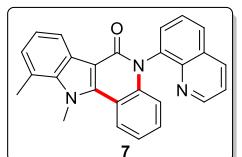
Prepared according to general procedure I . Purification of the crude product by flash column chromatography afforded the annulation product **5** as white solid in 86% yield (67 mg). ¹H NMR (CD₂Cl₂, 400 MHz, ppm): δ 8.74 (dd, $J = 4.1$, 1.5 Hz, 1 H), 8.43 (dd, $J = 8.1$, 1.4 Hz, 1 H), 8.35 (dd, $J = 8.3$, 1.5 Hz, 1 H), 8.21 (s, 1 H), 8.13-8.08 (m, 1 H), 7.84-7.79 (m, 2 H), 7.47-7.44 (m, 2 H), 7.29-7.20 (m, 3 H), 6.62 (dd, $J = 8.2$, 0.9 Hz, 1 H), 4.30 (s, 3H), 2.49 (s, 3 H); ¹³C NMR (CD₂Cl₂, 100 MHz, ppm) δ 160.4, 151.5, 145.2, 141.5, 140.4, 138.7, 136.9, 136.7, 131.8, 131.7, 130.2, 129.6, 128.6, 127.2, 126.3, 124.9, 123.3, 122.3, 121.9, 121.8, 117.7, 114.6,

109.3, 107.6, 34.1, 21.5; **HRMS**: calculated for C₂₆H₂₀N₃O [M+H⁺]: 390.1606; **found**: 390.1612.



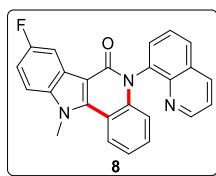
R_f = 0.55, 50 % EtOAc in hexanes

Prepared according to general procedure I . Purification of the crude product by flash column chromatography afforded the annulation product **6** as white solid in 78% yield (61 mg). **¹H NMR** (CD₂Cl₂, 400 MHz, ppm): δ 8.73 (d, J = 2.8 Hz, 1 H), 8.46 (dd, J = 8.2, 1.3 Hz, 1 H), 8.38 (d, J = 7.2 Hz, 1 H), 8.21 (d, J = 8.0 Hz, 1 H), 8.11-8.08 (m, 1 H), 7.82-7.78 (m, 2 H), 7.47 (dd, J = 8.3, 4.2, 1 H), 7.38 (s, 1 H), 7.28 (td, J = 7.2, 1.2 Hz, 1 H), 7.20 (td, J = 8.6, 1.5 Hz, 1 H), 7.15 (d, J = 7.9, 1 H), 6.59 (dd, J = 8.4, 1.0 Hz, 1 H), 4.33 (s, 3 H), 2.58 (s, 3 H); **¹³C NMR** (CDCl₃, 100 MHz, ppm) δ 160.5, 151.6, 145.1, 141.0, 140.5, 140.0, 136.5, 136.4, 134.7, 131.4, 130.0, 129.5, 128.2, 127.0, 123.8, 122.8, 122.5, 122.2, 122.0, 121.6, 117.8, 114.7, 109.2, 108.3, 33.75, 22.42; **HRMS**: calculated for C₂₆H₂₀N₃O [M+H⁺]: 390.1606; **found**: 390.1609.



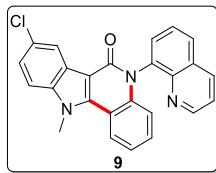
R_f = 0.55, 50 % EtOAc in hexanes

Prepared according to general procedure I . Purification of the crude product by flash column chromatography afforded the annulation product **7** as white solid in 44% yield (35 mg). **¹H NMR** (CDCl₃, 400 MHz, ppm): δ 8.77 (dd, J = 4.2, 1.7, 1 H), 8.41-8.39 (m, 1 H), 8.33-8.31 (m, 1 H), 8.27 (dd, J = 8.3, 1.6 Hz, 1 H), 8.03 (dd, J = 8.0, 1.6 Hz, 1 H), 7.81 (dd, J = 7.2, 1.6 Hz, 1 H), 7.76 (t, J = 7.9 Hz, 1 H), 7.41 (dd, J = 8.3, 4.2 Hz, 1 H), 7.25-7.18 (m, 4 H), 6.66-6.64 (m, 1 H), 4.49 (s, 3 H), 2.87 (s, 3 H); **¹³C NMR** (CDCl₃, 100 MHz, ppm) δ 160.4, 151.6, 145.1, 141.8, 141.2, 140.1, 136.5, 136.4, 131.3, 130.0, 129.4, 128.4, 128.1, 126.9, 125.8, 123.4, 122.2, 122.0, 121.5, 120.8, 120.7, 117.7, 114.3, 108.7, 37.2, 20.9; **HRMS**: calculated for C₂₆H₂₀N₃O [M+H⁺]: 390.1606; **found**: 390.1613.



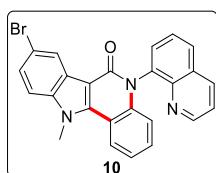
R_f = 0.50, 50 % EtOAc in hexanes

Prepared according to general procedure I . Purification of the crude product by flash column chromatography afforded the annulation product **8** as white solid in 84% yield (67 mg) with a bad solubility. **¹H NMR** (CDCl₃, 400 MHz, ppm): δ 8.79 (s, 1 H), 8.42 (d, J = 7.90 Hz, 1 H), 8.30 (d, J = 8.2 Hz, 1 H), 8.15 (d, J = 9.0 Hz, 1 H), 8.06 (d, J = 7.6 Hz, 1 H), 7.83-7.76 (m, 2 H), 7.44-7.43 (m, 2 H), 7.31-7.22 (m, 2 H), 7.18 (t, J = 7.8 Hz, 1 H), 6.67 (d, J = 8.1 Hz, 1 H), 4.36 (s, 3 H); **¹³C NMR** (CDCl₃, 100 MHz, ppm) δ 160.3, 159.9, 158.4, 151.7, 145.1, 141.3, 136.5, 136.5, 136.1, 131.3, 130.0, 129.6, 128.9, 127.0, 125.4, 125.3, 122.9, 122.1, 121.8, 117.9, 114.4, 112.9, 112.7, 109.9, 109.8, 108.1, 108.0, 107.8, 34.1; **HRMS**: calculated for C₂₅H₁₇FN₃O [M+H⁺]: 394.1356; **found**: 394.1368.



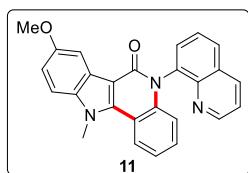
$R_f = 0.50$, 50 % EtOAc in hexanes

Prepared according to general procedure I . Purification of the crude product by flash column chromatography afforded the annulation product **9** as white solid in 87% yield (72 mg) with a bad solubility. **1H NMR** (CDCl_3 , 400 MHz, ppm): δ 8.79 (d, $J = 4.1$ Hz, 1 H), 8.49 (d, $J = 1.9$ Hz, 1 H), 8.43 (dd, $J = 7.0, 1.8$ Hz, 1 H), 8.30 (d, $J = 8.3$ Hz, 1 H), 8.07 (dd, $J = 7.6, 1.4$ Hz, 1 H), 7.82-7.77 (m, 2 H), 7.46-7.38 (m, 3 H), 7.31-7.26 (m, 2 H), 6.69 (dd, $J = 7.7, 1.5$ Hz, 1 H), 4.35 (s, 3 H); **13C NMR** (CDCl_3 , 100 MHz, ppm) δ 160.2, 151.7, 145.0, 141.3, 141.1, 138.4, 136.5, 136.1, 131.3, 130.0, 129.6, 129.0, 127.9, 127.0, 125.7, 124.9, 122.9, 122.1, 121.9, 117.9, 114.3, 110.1, 107.7, 34.1; **HRMS**: calculated for $\text{C}_{25}\text{H}_{17}\text{ClN}_3\text{O} [\text{M}+\text{H}^+]$: 410.1055; **found**: 410.1060.



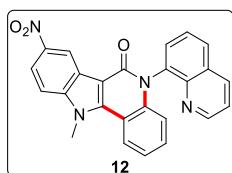
$R_f = 0.50$, 50 % EtOAc in hexanes

Prepared according to general procedure I . Purification of the crude product by flash column chromatography afforded the annulation product **10** as white solid in > 95% yield (89 mg) with a bad solubility. **1H NMR** (CDCl_3 , 400 MHz, ppm): δ 8.79 (dd, $J = 4.2, 1.6$ Hz, 1 H), 8.65 (d, $J = 1.9$ Hz, 1 H), 8.44-8.41 (m, 1 H), 8.30 (dd, $J = 8.3, 1.6$ Hz, 1 H), 8.07 (dd, $J = 7.5, 2.2$ Hz, 1 H), 7.83-7.77 (m, 2 H), 7.53-7.51 (m, 1 H), 7.44 (dd, $J = 8.3, 4.2$ Hz, 1 H), 7.40 (d, $J = 8.8$ Hz, 1 H), 7.31-7.24 (m, 2 H), 6.70-6.68 (m, 1 H), 4.35 (s, 3 H); **HRMS**: calculated for $\text{C}_{25}\text{H}_{17}\text{BrN}_3\text{O} [\text{M}+\text{H}^+]$: 456.0529; **found**: 456.0538.



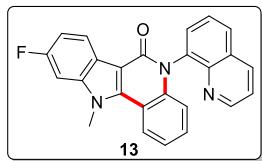
$R_f = 0.60$, 50 % EtOAc in hexanes

Prepared according to general procedure I . Purification of the crude product by flash column chromatography afforded the annulation product **11** as white solid in 68% yield (56 mg). **1H NMR** (CDCl_3 , 400 MHz, ppm): δ 8.80 (dd, $J = 4.2, 1.7$ Hz, 1 H), 8.41 (dd, $J = 8.1, 1.8$ Hz, 1 H), 8.29 (dd, $J = 8.3, 1.7$ Hz, 1 H), 8.05 (dd, $J = 8.1, 1.6$ Hz, 1 H), 8.01 (d, $J = 2.6$ Hz, 1 H), 7.83 (dd, $J = 7.2, 1.6$ Hz, 1 H), 7.78 (t, $J = 7.9$ Hz, 1 H), 7.44-7.40 (m, 2 H), 7.28-7.20 (m, 2 H), 7.07 (dd, $J = 9.0, 2.6$ Hz, 1 H), 6.66 (dd, $J = 8.1, 1.1$ Hz, 1 H), 4.32 (s, 3 H), 3.85 (s, 3 H); **13C NMR** (CDCl_3 , 100 MHz, ppm) δ 160.7, 155.8, 151.6, 145.2, 141.0, 140.2, 136.5, 136.4, 134.9, 131.4, 130.0, 129.4, 128.4, 127.0, 125.4, 122.8, 122.0, 121.7, 117.8, 115.3, 114.7, 110.0, 107.9, 103.2, 55.8, 33.9; **HRMS**: calculated for $\text{C}_{26}\text{H}_{20}\text{N}_3\text{O}_2 [\text{M}+\text{H}^+]$: 406.1556; **found**: 406.1554.



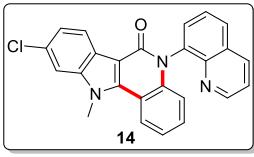
$R_f = 0.45$, 50 % EtOAc in hexanes

Prepared according to general procedure I . Purification of the crude product by flash column chromatography afforded the annulation product **12** as pale yellow solid in 45% yield (38 mg) with a bad solubility. **¹H NMR** (CDCl_3 , 400 MHz, ppm): δ 9.41 (d, $J = 2.3$ Hz, 1 H), 8.80 (dd, $J = 4.2, 1.7$ Hz, 1 H), 8.44-8.40 (m, 1 H), 8.34-8.30 (m, 2 H), 8.10 (dd, $J = 7.2, 2.5$ Hz, 1 H), 7.84-7.79 (m, 2 H), 7.59 (d, $J = 9.0$ Hz, 1 H), 7.46 (dd, $J = 8.3, 4.2$ Hz, 1 H), 7.34-7.31 (m, 2 H), 6.77-6.73 (m, 1 H), 4.42 (s, 3 H); **¹³C NMR** (CDCl_3 , 100 MHz, ppm) δ 151.7, 143.4, 142.8, 136.6, 131.2, 129.8, 129.7, 127.0, 124.3, 122.9, 122.2, 120.1, 119.3, 118.2, 109.3, 59.0, 34.5; **HRMS**: calculated for $\text{C}_{25}\text{H}_{17}\text{N}_4\text{O}_3$ [$\text{M}+\text{H}^+$]: 421.1301; **found**: 421.1308.



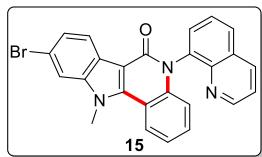
$R_f = 0.50$, 50 % EtOAc in hexanes

Prepared according to general procedure I . Purification of the crude product by flash column chromatography afforded the annulation product **13** as white solid in > 95% yield (76 mg) with a bad solubility. **¹H NMR** (CDCl_3 , 400 MHz, ppm): δ 8.79 (s, 1 H), 8.44 (d, $J = 7.8$ Hz, 2 H), 8.30 (d, $J = 8.4$ Hz, 1 H), 8.06 (d, $J = 7.5$ Hz, 1 H), 7.81-7.78 (m, 2 H), 7.43 (dd, $J = 6.9, 3.7$ Hz, 1 H), 7.26-7.20 (m, 3 H), 7.08 (t, $J = 8.6$ Hz, 1 H), 6.67 (d, $J = 8.4$ Hz, 1 H), 4.34 (s, 3 H); **¹³C NMR** (CDCl_3 , 100 MHz, ppm) δ 162.3, 160.7, 160.3, 151.7, 145.1, 141.0, 140.9, 140.6, 140.5, 136.5, 136.2, 131.3, 130.0, 129.6, 128.6, 127.0, 123.7, 122.7, 122.1, 121.9, 121.1, 117.9, 114.4, 110.7, 110.5, 108.3, 96.2, 96.1, 34.1; **HRMS**: calculated for $\text{C}_{25}\text{H}_{17}\text{FN}_3\text{O}$ [$\text{M}+\text{H}^+$]: 394.1350; **found**: 394.1356.



$R_f = 0.50$, 50 % EtOAc in hexanes

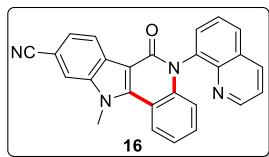
Prepared according to general procedure I . Purification of the crude product by flash column chromatography afforded the annulation product **14** as white solid in 77% yield (64 mg) with a bad solubility. **¹H NMR** (CDCl_3 , 400 MHz, ppm): δ 8.79 (dd, $J = 4.2, 1.6$ Hz, 1 H), 8.43 (dd, $J = 8.1, 1.9$ Hz, 1 H), 8.40 (d, $J = 8.4$ Hz, 1 H), 8.30 (dd, $J = 8.3, 1.6$ Hz, 1 H), 8.06 (dd, $J = 7.7, 1.9$ Hz, 1 H), 7.83-7.76 (m, 2 H), 7.54 (d, $J = 1.6$ Hz, 1 H), 7.43 (dd, $J = 8.3, 4.2$ Hz, 1 H), 7.32-7.23 (m, 3 H), 6.68 (dd, $J = 7.9, 1.7$ Hz, 1 H), 4.35 (s, 3 H); **¹³C NMR** (CDCl_3 , 100 MHz, ppm) δ 160.2, 151.7, 145.0, 141.2, 140.9, 140.6, 136.5, 136.1, 131.3, 130.6, 130.0, 129.6, 128.9, 127.0, 123.5, 123.3, 122.9, 122.8, 122.1, 121.9, 117.9, 114.3, 109.4, 34.0; **HRMS**: calculated for $\text{C}_{25}\text{H}_{17}\text{FN}_3\text{O}$ [$\text{M}+\text{H}^+$]: 410.1055; **found**: 410.1054.



$R_f = 0.50$, 50 % EtOAc in hexanes

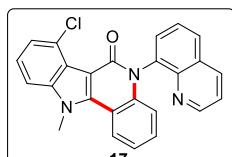
Prepared according to general procedure I . Purification of the crude product by flash column chromatography afforded the annulation product **15** as white solid in 92% yield (84 mg) with a bad solubility. **¹H NMR** (CDCl_3 , 400 MHz, ppm): δ 8.79 (dd, $J = 4.2, 1.7$ Hz, 1 H), 8.43 (dd, $J = 8.2, 2.0$ Hz, 1 H), 8.35 (d, $J = 8.4$ Hz, 1 H), 8.30 (dd, $J = 8.4, 1.7$ Hz, 1 H), 8.06 (dd, $J = 7.7, 2.0$ Hz, 1 H), 7.83-7.76 (m, 2 H), 7.70 (d, J

= 1.4 Hz, 1 H), 7.45-7.42 (m, 2 H), 7.30-7.25 (m, 2 H), 6.68-6.66 (m, 1 H), 4.34 (s, 3 H); **¹³C NMR** (CDCl₃, 100 MHz, ppm) δ 151.7, 145.0, 141.3, 140.9, 136.5, 136.1, 131.3, 130.0, 129.6, 128.9, 127.0, 125.4, 123.8, 123.7, 122.9, 122.1, 121.9, 118.4, 118.0, 114.3, 112.4, 34.0; **HRMS**: calculated for C₂₅H₁₇BrN₃O [M+H⁺]: 456.0529; **found**: 456.0549.



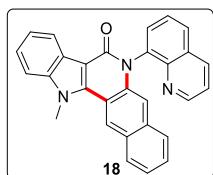
R_f = 0.45, 50 % EtOAc in hexanes

Prepared according to general procedure I . Purification of the crude product by flash column chromatography afforded the annulation product **12** as white solid in 77% yield (62 mg) with a bad solubility. **¹H NMR** (CDCl₃, 400 MHz, ppm): δ 8.79 (dd, J = 4.1, 1.5 Hz, 1 H), 8.57 (d, J = 8.2 Hz, 1 H), 8.47-8.44 (m, 1 H), 8.31 (dd, J = 8.3, 1.4, 1 H), 8.17 (s, 1 H), 8.08 (dd, J = 7.2, 2.3 Hz, 1 H), 7.86 (s, 1 H), 7.83-7.76 (m, 2 H), 7.58 (d, J = 8.2 Hz, 1 H), 6.71-6.88 (m, 1 H), 4.41 (s, 3 H); **¹³C NMR** (CDCl₃, 100 MHz, ppm) δ 160.0, 151.6, 142.8, 141.8, 139.0, 131.4, 130.1, 129.9, 129.8, 128.1, 127.1, 125.2, 123.3, 123.2, 122.3, 120.3, 118.1, 113.9, 113.8, 108.3, 107.2, 34.2; **HRMS**: calculated for C₂₆H₁₇N₄O [M+H⁺]: 401.1397; **found**: 410.1402.



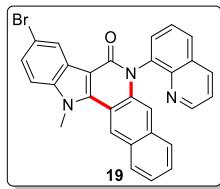
R_f = 0.65, 50 % EtOAc in hexanes

Prepared according to general procedure I . Purification of the crude product by flash column chromatography afforded the annulation product **17** as white solid in 72% yield (59 mg) with a bad solubility. **¹H NMR** (CDCl₃, 400 MHz, ppm): δ 8.78 (dd, J = 4.2, 1.7 Hz, 1 H), 8.43-8.41 (m, 1 H), 8.27 (dd, J = 8.3, 1.7 Hz, 1 H), 8.02 (dd, J = 8.2, 1.5 Hz, 1 H), 7.83 (dd, J = 7.3, 1.5 Hz, 1 H), 7.76 (t, J = 8.0 Hz, 1 H), 7.44 (dd, J = 7.2, 2.0 Hz, 1 H), 7.41 (t, J = 4.1 Hz, 1 H), 7.36-7.31 (m, 2 H), 7.24-7.21 (m, 2 H), 6.58-6.55 (m, 1 H), 4.36 (s, 3 H); **¹³C NMR** (CDCl₃, 100 MHz, ppm) δ 158.9, 151.5, 145.0, 141.9, 141.7, 136.7, 136.5, 131.5, 131.0, 130.1, 129.3, 129.1, 128.3, 127.1, 125.0, 124.7, 123.4, 123.0, 122.0, 121.5, 117.5, 113.5, 107.9, 34.6; **HRMS**: calculated for C₂₅H₁₇ClN₃O [M+H⁺]: 410.1060; **found**: 410.1075.



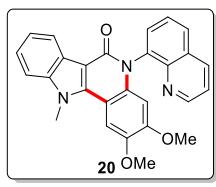
R_f = 0.70, 50 % EtOAc in hexanes

Prepared according to general procedure I . Purification of the crude product by flash column chromatography afforded the annulation product **18** as white solid in 67% yield (57 mg) with a bad solubility. **¹H NMR** (CD₂Cl₂, 400 MHz, ppm): δ 8.96 (s, 1 H), 8.70 (s, 1 H), 8.44 (s, 1 H), 8.39 (d, J = 19.6 Hz, 1 H), 8.18 (s, 1 H), 8.04 (d, J = 7.6 Hz, 1 H), 7.96 (d, J = 19.2 Hz, 1 H), 7.88 (d, J = 6.8 Hz, 1 H), 7.65 (d, J = 8.0 Hz, 1 H), 7.49-7.43 (m, 5 H), 7.31 (s, 1 H), 6.99 (s, 1H), 4.51 (s, 3 H); **HRMS**: calculated for C₂₉H₂₀N₃O [M+H⁺]: 426.1601; **found**: 426.1605.



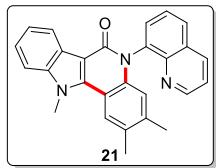
$R_f = 0.65$, 50 % EtOAc in hexanes

Prepared according to general procedure I . Purification of the crude product by flash column chromatography afforded the annulation product **19** as white solid in 92% yield (93 mg) with a bad solubility. **1H NMR** (CD_2Cl_2 , 400 MHz, ppm): δ 8.92 (s, 1 H), 8.61 (s, 1 H), 8.58-8.46 (m, 2 H), 8.18 (s, 1 H), 8.04 (s, 1 H), 7.96 (s, 1 H), 7.87 (s, 1 H), 7.55-7.44 (m, 6 H), 7.98 (s, 1 H), 4.44 (s, 3 H); **HRMS**: calculated for $\text{C}_{29}\text{H}_{19}\text{BrN}_3\text{O} [\text{M}+\text{H}^+]$: 504.0706; **found**: 504.0711



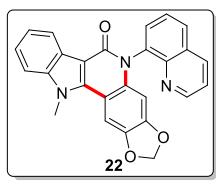
$R_f = 0.45$, 50 % EtOAc in hexanes

Prepared according to general procedure I . Purification of the crude product by flash column chromatography afforded the annulation product **20** as white solid in 46% yield (41 mg). **1H NMR** (CDCl_3 , 400 MHz, ppm): δ 8.81 (dd, $J = 4.2, 1.7$ Hz, 1 H), 8.47 (d, $J = 7.7$ Hz, 1 H), 8.29 (dd, $J = 8.3, 1.6$ Hz, 1 H), 8.05 (dd, $J = 8.2, 1.4$ Hz, 1 H), 7.87-7.84 (m, 2 H), 7.78 (t, $J = 7.9$ Hz, 1 H), 7.50 (d, $J = 8.3$ Hz, 1 H), 7.45-7.40 (m, 2 H), 7.32 (t, $J = 7.8$ Hz, 1 H), 6.13 (s, 1 H), 4.35 (s, 3H), 4.00 (s, 3H), 3.42 (s, 3 H); **13C NMR** (CDCl_3 , 100 MHz, ppm) δ 160.3, 151.7, 150.4, 145.0, 145.0, 144.8, 140.7, 139.9, 137.1, 136.5, 131.4, 129.9, 129.5, 126.9, 125.0, 124.2, 122.4, 122.1, 122.0, 108.8, 107.2, 107.1, 105.5, 101.1, 56.8, 55.7, 33.5; **HRMS**: calculated for $\text{C}_{27}\text{H}_{22}\text{N}_3\text{O}_3 [\text{M}+\text{H}^+]$: 436.1661; **found**: 436.1664.



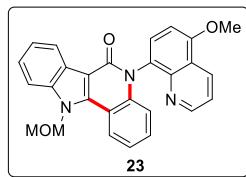
$R_f = 0.45$, 50 % EtOAc in hexanes

Prepared according to general procedure I . Purification of the crude product by flash column chromatography afforded the annulation product **21** as white solid in 47% yield (38 mg) with a bad solubility. **1H NMR** (CDCl_3 , 400 MHz, ppm): δ 8.80 (dd, $J = 4.1, 1.5$ Hz, 1 H), 8.49 (d, $J = 7.8$ Hz, 1 H), 8.29 (dd, $J = 8.3, 1.6$ Hz, 1 H), 8.19 (s, 1 H), 8.05 (dd, $J = 7.5, 2.2$ Hz, 1 H), 7.81-7.76 (m, 2 H), 7.53-7.51 (m, 1 H), 7.46-7.40 (m, 2 H), 7.32 (t, $J = 7.1$ Hz, 1 H), 6.44 (s, 1 H), 4.37 (s, 3 H), 2.38 (s, 3 H), 2.10 (s, 3 H); **13C NMR** (CDCl_3 , 100 MHz, ppm) δ 160.5, 151.6, 145.3, 140.5, 140.0, 139.7, 138.1, 136.6, 136.4, 131.4, 130.3, 130.0, 129.3, 126.9, 125.0, 124.3, 123.3, 122.6, 122.0, 121.9, 118.4, 112.5, 108.9, 107.8, 33.8, 20.5, 19.9; **HRMS**: calculated for $\text{C}_{27}\text{H}_{22}\text{N}_3\text{O} [\text{M}+\text{H}^+]$: 404.1757; **found**: 404.1763.



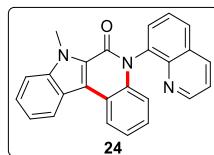
$R_f = 0.55$, 50 % EtOAc in hexanes

Prepared according to general procedure I . Purification of the crude product by flash column chromatography afforded the annulation product **22** as white solid in 72% yield (61 mg) with a bad solubility. **¹H NMR** (CDCl_3 , 400 MHz, ppm): δ 8.81 (dd, $J = 4.1, 1.6$ Hz, 1 H), 8.46 (d, $J = 7.8$ Hz, 1 H), 8.29 (dd, $J = 8.3, 1.6$ Hz, 1 H), 8.05 (dd, $J = 7.8, 2.0$ Hz, 1 H), 7.87 (s, 1 H), 7.82-7.75 (m, 2 H), 7.50 (d, $J = 8.3$ Hz, 1 H), 7.45-7.41 (m, 2 H), 7.34-7.30 (m, 1 H), 6.15 (s, 1 H), 5.79 (dd, $J = 12.7, 1.2$ Hz, 2 H), 4.31 (s, 3 H); **¹³C NMR** (CDCl_3 , 100 MHz, ppm) δ 161.2, 151.7, 149.5, 143.5, 140.9, 136.5, 131.3, 129.6, 127.0, 124.4, 122.4, 122.1, 108.8, 101.9, 101.4, 98.9, 33.6; **HRMS**: calculated for $\text{C}_{26}\text{H}_{18}\text{N}_3\text{O}_3$ [$\text{M}+\text{H}^+$]: 420.1343; **found**: 420.1366.



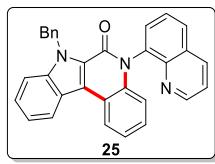
$R_f = 0.60$, 50 % EtOAc in hexanes

A mixture of amide **23a** (72 mg, 0.2 mmol, 1 equiv.), $\text{Cu}(\text{OAc})_2$ (27 mg, 0.15 mmol, 0.75 equiv.), TBAI (111 mg, 0.3 mmol, 1.5 equiv.), CsF (36.5 mg, 1.2 equiv.), and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (120 mg, 2 equiv.) in DMF (1.0 mL)/MeCN (1.0 mL) in a 10 mL glass vial (purged with O_2 , sealed with PTFE cap) was heated at 100 °C for 2 hour. The reaction mixture was cooled to RT. The resulting residue was purified by silica gel flash chromatography to give the annulation product **23** in 62% (54 mg) isolated yield ($R_f = 0.4$, 50% EtOAc in hexanes). **¹H NMR** (CDCl_3 , 400 MHz, ppm): δ 8.77 (dd, $J = 4.2, 1.7$ Hz, 1 H), 8.68 (dd, $J = 8.5, 1.8$ Hz, 1 H), 8.54-8.50 (m, 2 H), 7.70 (d, $J = 8.2$ Hz, 1 H), 7.65 (d, $J = 8.3$ Hz, 1H), 7.46 (td, $J = 7.8, 1.3$ Hz, 1 H), 7.41-7.33 (m, 2 H), 7.31-7.23 (m, 2 H), 7.06 (d, $J = 8.2$ Hz, 1 H), 6.76-6.73 (m, 1 H), 5.97 (dd, $J = 14.8, 12.0$ Hz, 2 H), 4.12 (s, 3 H), 3.47 (s, 3 H); **¹³C NMR** (CDCl_3 , 100 MHz, ppm) δ 160.7, 156.1, 151.8, 145.5, 141.5, 140.9, 140.5, 131.4, 131.1, 128.9, 128.4, 125.1, 125.0, 124.1, 122.9, 122.6, 122.24, 122.16, 121.1, 117.7, 113.9, 113.6, 109.8, 109.0, 104.5, 75.6, 56.5, 56.2; **HRMS**: calculated for $\text{C}_{27}\text{H}_{22}\text{N}_3\text{O}_3$ [$\text{M}+\text{H}^+$]: 436.1661; **found**: 436.1661.



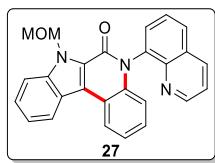
$R_f = 0.50$, 50 % EtOAc in hexanes

Prepared according to general procedure II. Purification of the crude product by flash column chromatography afforded the annulation product **24** as white solid in 63% yield (48 mg). **¹H NMR** (CDCl_3 , 400 MHz, ppm): δ 8.81 (dd, $J = 4.2, 1.7$ Hz, 1 H), 8.56 (dd, $J = 8.0, 1.2$ Hz, 1 H), 8.51 (d, $J = 8.2$ Hz, 1 H), 8.30 (dd, $J = 8.4, 1.7$ Hz, 1 H), 8.06 (dd, $J = 7.8, 1.8$ Hz, 1 H), 7.82 (dd, $J = 7.3, 1.9$ Hz, 1 H), 7.78 (t, $J = 7.5$ Hz, 1H), 7.61-7.55 (m, 2 H), 7.44 (t, $J = 4.1$ Hz, 1 H), 7.42-7.39 (m, 1 H), 7.36-7.32 (m, 1 H), 7.15-7.11 (m, 1 H), 6.55 (dd, $J = 8.5, 0.8$ Hz, 1 H), 4.38 (s, 3 H); **¹³C NMR** (CDCl_3 , 100 MHz, ppm) δ 157.6, 151.7, 144.9, 141.1, 138.0, 136.5, 136.3, 131.0, 129.9, 129.6, 126.9, 126.5, 126.2, 125.9, 123.7, 123.0, 122.7, 122.3, 122.1, 121.2, 119.9, 119.7, 116.9, 110.8, 31.7; **HRMS**: calculated for $\text{C}_{25}\text{H}_{18}\text{N}_3\text{O}$ [$\text{M}+\text{H}^+$]: 376.1450; **found**: 376.1452.



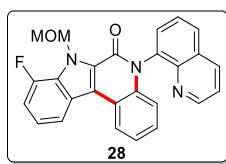
$R_f = 0.50$, 50 % EtOAc in hexanes

Prepared according to general procedure II. Purification of the crude product by flash column chromatography afforded the annulation product **25** as white solid in 64% yield (57 mg). **1H NMR** (CDCl_3 , 400 MHz, ppm): δ 8.79 (dd, $J = 4.2, 1.7$ Hz, 1 H), 8.59 (dd, $J = 8.0, 1.1$ Hz, 1 H), 8.53 (d, $J = 8.1$ Hz, 1 H), 8.28 (dd, $J = 8.4, 1.6$ Hz, 1 H), 8.04 (dd, $J = 8.1, 1.4$ Hz, 1 H), 7.83 (dd, $J = 7.2, 1.5$ Hz, 1 H), 7.76 (t, $J = 7.6$ Hz, 1 H), 7.54 (d, $J = 8.2$ Hz, 1 H), 7.49 (td, $J = 6.9, 0.8$ Hz, 1 H), 7.44-7.39 (m, 2 H), 7.38-7.33 (m, 1 H), 7.23-7.13 (m, 6 H), 6.60-6.57 (m, 1 H), 6.31 (d, $J = 16.1$ Hz, 1 H), 6.10 (d, $J = 16.1$ Hz, 1 H); **13C NMR** (CDCl_3 , 100 MHz, ppm) δ 157.3, 151.6, 144.9, 140.7, 138.4, 138.1, 136.5, 136.2, 131.1, 130.0, 129.6, 128.6, 127.1, 126.9, 126.4, 126.2, 126.1, 123.8, 123.1, 122.8, 122.7, 122.1, 121.5, 120.4, 119.6, 116.9, 111.7, 48.1; **HRMS**: calculated for $\text{C}_{31}\text{H}_{22}\text{N}_3\text{O}$ [$\text{M}+\text{H}^+$]: 452.1763; **found**: 452.1774.



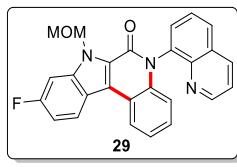
$R_f = 0.55$, 50 % EtOAc in hexanes

Prepared according to general procedure II. Purification of the crude product by flash column chromatography afforded the annulation product **27** as white solid in 65% yield (53 mg). **1H NMR** (CDCl_3 , 400 MHz, ppm): δ 8.77 (dd, $J = 4.2, 1.7$ Hz, 1 H), 8.58 (dd, $J = 8.1, 1.1$ Hz, 1 H), 8.51 (d, $J = 8.1$ Hz, 1 H), 8.27 (dd, $J = 8.3, 1.6$ Hz, 1 H), 8.05 (dd, $J = 8.1, 1.6$ Hz, 1 H), 7.82 (dd, $J = 7.3, 1.6$ Hz, 1 H), 7.77 (t, $J = 7.6$ Hz, 2 H), 7.57 (td, $J = 7.2, 0.8$ Hz, 1 H), 7.45-7.40 (m, 2 H), 7.36-7.32 (m, 1 H), 7.18-7.14 (m, 1 H), 6.58 (dd, $J = 8.6, 0.6$ Hz, 1 H), 6.42 (d, $J = 10.4$ Hz, 1 H), 6.23 (d, $J = 10.4$ Hz, 1 H), 3.35 (s, 3 H); **13C NMR** (CDCl_3 , 100 MHz, ppm) δ 157.0, 151.6, 144.8, 140.9, 138.2, 136.5, 136.1, 131.0, 129.9, 129.6, 126.9, 126.8, 126.5, 126.4, 123.9, 123.0, 122.9, 122.8, 122.1, 122.1, 121.3, 119.3, 116.9, 112.1, 55.9; **HRMS**: calculated for $\text{C}_{26}\text{H}_{19}\text{N}_3\text{NaO}_2$ [$\text{M}+\text{Na}^+$]: 428.1375; **found**: 428.1372.



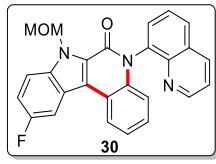
$R_f = 0.50$, 50 % EtOAc in hexanes

Prepared according to general procedure II. Purification of the crude product by flash column chromatography afforded the annulation product **28** as white solid in 41% yield (35 mg). **1H NMR** (CDCl_3 , 400 MHz, ppm): δ 8.77 (dd, $J = 4.2, 1.7$ Hz, 1 H), 8.56 (dd, $J = 8.0, 1.2$ Hz, 1 H), 8.31 (d, $J = 1.6$ Hz, 1 H), 8.29 (d, $J = 1.7$ Hz, 1 H), 8.07 (dd, $J = 8.0, 1.7$ Hz, 1 H), 7.83 (dd, $J = 7.3, 1.7$ Hz, 1 H), 7.79 (t, $J = 7.6$ Hz, 1 H), 7.44 (dd, $J = 8.3, 4.2$ Hz, 1 H), 7.38-7.28 (m, 3 H), 7.21-7.17 (m, 1 H), 6.60 (dd, $J = 8.5, 0.8$ Hz, 1 H), 6.53 (d, $J = 10.4$ Hz, 1 H), 6.37 (d, $J = 10.4$ Hz, 1 H), 3.36 (s, 3 H); **13C NMR** (CDCl_3 , 100 MHz, ppm) δ 156.9, 152.2, 151.6, 149.8, 144.7, 138.4, 136.5, 135.9, 131.0, 130.0, 129.7, 128.9, 128.8, 127.2, 126.9, 126.7, 126.7, 123.9, 122.9, 122.2, 122.1, 121.8, 118.9, 118.9, 117.0, 112.8, 112.6, 56.0; **HRMS**: calculated for $\text{C}_{26}\text{H}_{18}\text{FN}_3\text{NaO}_2$ [$\text{M}+\text{Na}^+$]: 446.1281; **found**: 446.1288.



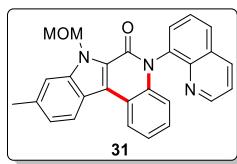
$R_f = 0.50$, 50 % EtOAc in hexanes

Prepared according to general procedure II. Purification of the crude product by flash column chromatography afforded the annulation product **29** as white solid in 62% yield (53 mg). **1H NMR** (CDCl_3 , 400 MHz, ppm): δ 8.77 (dd, $J = 4.2, 1.7$ Hz, 1 H), 8.41 (dd, $J = 7.9, 1.2$ Hz, 1 H), 8.28 (dd, $J = 8.4, 1.7$ Hz, 1 H), 8.12 (dd, $J = 9.6, 2.6$ Hz, 1 H), 8.06 (dd, $J = 8.0, 1.7$ Hz, 1 H), 7.82 (dd, $J = 7.3, 1.7$ Hz, 1 H), 7.77 (t, $J = 7.6$ Hz, 1 H), 7.72 (dd, $J = 9.1, 4.5$ Hz, 1 H), 7.42 (dd, $J = 8.3, 4.2$ Hz, 1 H), 7.37-7.29 (m, 2 H), 7.18-7.14 (m, 1 H), 6.58 (dd, $J = 8.4, 0.7$ Hz, 1 H), 6.38 (d, $J = 10.8$ Hz, 1 H), 6.19 (d, $J = 10.6$ Hz, 1 H), 3.34 (s, 3 H); **13C NMR** (CDCl_3 , 100 MHz, ppm) δ 163.5, 161.1, 156.7, 151.6, 144.7, 141.7, 141.6, 138.3, 136.5, 135.9, 131.00, 129.9, 129.7, 126.9, 126.8, 124.3, 124.2, 123.7, 122.8, 122.2, 121.4, 119.5, 118.8, 117.0, 111.3, 111.0, 98.7, 98.4, 75.2, 56.0; **HRMS**: calculated for $\text{C}_{26}\text{H}_{18}\text{FN}_3\text{NaO}_2$ [$\text{M}+\text{Na}^+$]: 446.1281; **found**: 446.1291.



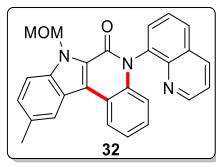
$R_f = 0.50$, 50 % EtOAc in hexanes

Prepared according to general procedure II. Purification of the crude product by flash column chromatography afforded the annulation product **30** as white solid in 56% yield (48 mg). **1H NMR** (CDCl_3 , 400 MHz, ppm): δ 8.77 (dd, $J = 4.2, 1.7$ Hz, 1 H), 8.50 (dd, $J = 8.0, 1.1$ Hz, 1 H), 8.43 (dd, $J = 8.9, 5.2$ Hz, 1 H), 8.30 (dd, $J = 8.4, 1.6$ Hz, 1 H), 8.06 (dd, $J = 7.9, 1.7$ Hz, 1 H), 7.82 (dd, $J = 7.3, 1.8$ Hz, 1 H), 7.78 (t, $J = 7.5$ Hz, 1 H), 7.46-7.42 (m, 2 H), 7.36-7.32 (m, 1 H), 7.21-7.15 (m, 2 H), 6.59-6.57 (m, 1 H), 6.37 (d, $J = 10.6$ Hz, 1 H), 6.15 (d, $J = 10.6$ Hz, 1 H), 3.36 (s, 3 H); **13C NMR** (CDCl_3 , 100 MHz, ppm) δ 160.0, 157.7, 156.9, 151.6, 144.7, 138.1, 137.3, 136.5, 135.9, 131.0, 130.0, 129.7, 127.4, 126.9, 126.6, 123.5, 123.0, 122.9, 122.8, 122.2, 120.9, 120.8, 118.9, 117.0, 115.5, 115.3, 113.1, 113.0, 108.1, 107.8, 75.1, 55.9; **HRMS**: calculated for $\text{C}_{26}\text{H}_{18}\text{FN}_3\text{NaO}_2$ [$\text{M}+\text{Na}^+$]: 446.1281; **found**: 446.1291.



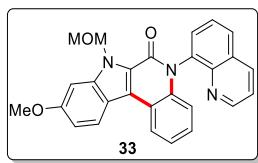
$R_f = 0.55$, 50 % EtOAc in hexanes

Prepared according to general procedure II. Purification of the crude product by flash column chromatography afforded the annulation product **31** as white solid in 66% yield (56 mg). **1H NMR** (CDCl_3 , 400 MHz, ppm): δ 8.77 (dd, $J = 4.2, 1.6$ Hz, 1 H), 8.55 (dd, $J = 8.0, 1.0$ Hz, 1 H), 8.34 (d, $J = 8.3$ Hz, 1 H), 8.28 (dd, $J = 8.4, 1.7$ Hz, 1 H), 8.05 (dd, $J = 8.0, 1.6$ Hz, 1 H), 7.82 (dd, $J = 7.2, 1.6$ Hz, 1 H), 7.77 (t, $J = 7.6$ Hz, 1 H), 7.57 (s, 1 H), 7.42 (dd, $J = 8.3, 4.2$ Hz, 1 H), 7.35-7.32 (m, 1 H), 7.27 (d, $J = 8.2$ Hz, 1 H), 7.17-7.13 (m, 1 H), 6.57 (d, $J = 8.2$ Hz, 1 H), 6.39 (d, $J = 10.6$ Hz, 1 H), 6.20 (d, $J = 10.6$ Hz, 1 H), 3.36 (s, 3 H), 2.60 (s, 3 H); **13C NMR** (CDCl_3 , 100 MHz, ppm) δ 157.0, 151.6, 144.8, 141.3, 138.2, 137.2, 136.5, 136.1, 131.0, 129.9, 129.6, 126.9, 126.4, 126.0, 124.0, 124.0, 122.7, 122.6, 122.1, 121.4, 120.8, 119.3, 116.9, 111.8, 74.9, 55.9, 22.3; **HRMS**: calculated for $\text{C}_{27}\text{H}_{21}\text{N}_3\text{NaO}_2$ [$\text{M}+\text{Na}^+$]: 442.1531; **found**: 442.1541.



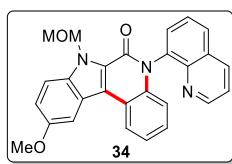
$R_f = 0.50$, 50 % EtOAc in hexanes

Prepared according to general procedure II. Purification of the crude product by flash column chromatography afforded the annulation product **32** as white solid in 71% yield (63 mg). **1H NMR** (CDCl_3 , 400 MHz, ppm): δ 8.77 (dd, $J = 4.0, 1.4$ Hz, 1 H), 8.58 (d, $J = 7.9$ Hz, 1 H), 8.28-8.26 (m, 2 H), 8.04 (dd, $J = 8.0, 1.2$ Hz, 1 H), 7.82-7.81 (m, 1 H), 7.77 (t, $J = 7.6$ Hz, 1 H), 7.66 (d, $J = 8.5$ Hz, 1 H), 7.43-7.39 (m, 2 H), 7.34 (t, $J = 7.5$ Hz, 1 H), 7.16-7.13 (m, 1 H), 6.57 (d, $J = 8.4$ Hz, 1 H), 6.38 (d, $J = 10.5$ Hz, 1 H), 6.19 (d, $J = 10.6$ Hz, 1 H), 3.33 (s, 3 H), 2.61 (s, 3 H); **13C NMR** (CDCl_3 , 100 MHz, ppm) δ 157.1, 151.6, 144.8, 139.3, 138.1, 136.5, 136.1, 131.4, 131.0, 129.9, 129.6, 128.5, 126.9, 126.4, 126.3, 123.9, 123.1, 122.7, 122.5, 122.1, 120.8, 119.4, 116.9, 111.7, 74.9, 55.9, 21.9; **HRMS**: calculated for $\text{C}_{27}\text{H}_{21}\text{N}_3\text{NaO}_2$ [$\text{M}+\text{Na}^+$]: 442.1531; **found**: 442.1538.



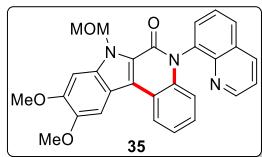
$R_f = 0.55$, 50 % EtOAc in hexanes

Prepared according to general procedure II. Purification of the crude product by flash column chromatography afforded the annulation product **33** as white solid in 64% yield (56 mg). **1H NMR** (CDCl_3 , 400 MHz, ppm): δ 8.78 (dd, $J = 4.2, 1.7$ Hz, 1 H), 8.50 (dd, $J = 8.0, 1.1$ Hz, 1 H), 8.33 (d, $J = 8.9$ Hz, 1 H), 8.27 (dd, $J = 8.4, 1.7$ Hz, 1 H), 8.04 (dd, $J = 8.1, 1.6$ Hz, 1 H), 7.82 (dd, $J = 7.3, 1.6$ Hz, 1 H), 7.76 (t, $J = 7.6$ Hz, 1 H), 7.41 (dd, $J = 8.3, 4.2$ Hz, 1 H), 7.33-7.29 (m, 1 H), 7.16-7.12 (m, 2 H), 7.04 (dd, $J = 8.9, 2.3$ Hz, 1 H), 6.56 (d, $J = 7.8$ Hz, 1 H), 6.37 (d, $J = 10.6$ Hz, 1 H), 6.16 (d, $J = 10.4$ Hz, 1 H), 3.94 (s, 3 H), 3.36 (s, 3 H); **13C NMR** (CDCl_3 , 100 MHz, ppm) δ 159.6, 156.8, 151.5, 144.8, 142.4, 138.2, 136.5, 136.1, 131.0, 129.9, 129.6, 126.9, 126.4, 125.6, 123.8, 123.7, 122.6, 122.1, 121.7, 119.0, 116.9, 116.8, 112.8, 94.2, 74.9, 55.8, 55.7; **HRMS**: calculated for $\text{C}_{27}\text{H}_{21}\text{N}_3\text{NaO}_3$ [$\text{M}+\text{Na}^+$]: 458.1481; **found**: 458.1493.



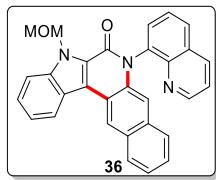
$R_f = 0.50$, 50 % EtOAc in hexanes

Prepared according to general procedure II. Purification of the crude product by flash column chromatography afforded the annulation product **34** as white solid in 68% yield (60 mg). **1H NMR** (CDCl_3 , 400 MHz, ppm): δ 8.78 (dd, $J = 4.2, 1.6$ Hz, 1 H), 8.50 (dd, $J = 7.9, 0.8$ Hz, 1 H), 8.29 (dd, $J = 8.4, 1.6$ Hz, 1 H), 8.06 (dd, $J = 8.0, 1.6$ Hz, 1 H), 7.89 (d, $J = 2.2$ Hz, 1 H), 7.83 (dd, $J = 7.8, 1.6$ Hz, 1 H), 7.78 (t, $J = 7.6$ Hz, 1 H), 7.70 (d, $J = 9.0$ Hz, 1 H), 7.40 (dd, $J = 8.3, 4.2$ Hz, 1 H), 7.38-7.34 (m, 1 H), 7.25 (dd, $J = 9.0, 2.3$ Hz, 1 H), 7.18-7.13 (m, 1 H), 6.58 (d, $J = 7.9$ Hz, 1 H), 6.40 (d, $J = 10.6$ Hz, 1 H), 6.20 (d, $J = 10.6$ Hz, 1 H), 4.02 (s, 3 H), 3.34 (s, 3 H); **13C NMR** (CDCl_3 , 100 MHz, ppm) δ 157.6, 155.6, 151.6, 144.8, 138.1, 136.5, 136.1, 131.0, 129.9, 129.6, 126.9, 126.7, 126.2, 123.6, 123.2, 122.7, 122.2, 120.7, 119.4, 117.0, 116.97, 112.9, 104.6, 75.05, 56.2, 55.9; **HRMS**: calculated for $\text{C}_{27}\text{H}_{21}\text{N}_3\text{NaO}_3$ [$\text{M}+\text{Na}^+$]: 458.1481; **found**: 458.1493.



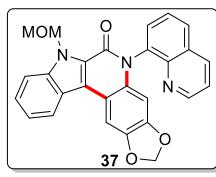
$R_f = 0.50$, 50 % EtOAc in hexanes

Prepared according to general procedure II. Purification of the crude product by flash column chromatography afforded the annulation product **35** as white solid in 85% yield (79 mg). **1H NMR** (CDCl_3 , 400 MHz, ppm): δ 8.79 (dd, $J = 4.2, 1.7$ Hz, 1 H), 8.43 (dd, $J = 8.0, 1.0$ Hz, 1 H), 8.28 (dd, $J = 8.4, 1.7$ Hz, 1 H), 8.05 (dd, $J = 8.0, 1.6$ Hz, 1 H), 7.83 (dd, $J = 7.3, 1.6$ Hz, 1 H), 7.79-7.76 (m, 2 H), 7.42 (dd, $J = 8.3, 4.2$ Hz, 1 H), 7.35-7.31 (m, 1 H), 7.18 (s, 1 H), 7.14 (td, $J = 7.9, 1.3$ Hz, 1 H), 6.57-6.55 (m, 1 H), 6.37 (d, $J = 10.8$ Hz, 1 H), 6.16 (d, $J = 10.8$ Hz, 1 H), 4.08 (s, 3 H), 4.04 (s, 3 H), 3.34 (s, 3 H); **13C NMR** (CDCl_3 , 100 MHz, ppm) δ 156.8, 151.5, 150.7, 146.7, 144.9, 138.2, 136.5, 136.4, 136.2, 131.1, 129.9, 129.6, 126.9, 126.2, 125.2, 123.5, 122.6, 122.1, 121.3, 119.2, 116.9, 115.3, 103.7, 94.1, 75.0, 56.7, 56.3, 55.8; **HRMS**: calculated for $\text{C}_{28}\text{H}_{23}\text{N}_3\text{NaO}_4$ [$\text{M}+\text{Na}^+$]: 488.1586; **found**: 488.1595.



$R_f = 0.50$, 50 % EtOAc in hexanes

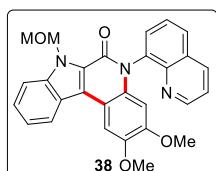
Prepared according to general procedure II. Purification of the crude product by flash column chromatography afforded the annulation product **36** as white solid in 62% yield (57 mg). **1H NMR** (CDCl_3 , 400 MHz, ppm): δ 9.02 (s, 1 H), 8.75 (dd, $J = 4.1, 1.6$ Hz, 1 H), 8.69 (d, $J = 8.1$ Hz, 1 H), 8.32 (dd, $J = 8.3, 1.6$ Hz, 1 H), 8.11 (dd, $J = 8.2, 1.5$ Hz, 1 H), 8.03 (d, $J = 8.2$ Hz, 1 H), 7.90 (dd, $J = 7.2, 1.5$ Hz, 1 H), 7.85 (d, $J = 8.0$ Hz, 1 H), 7.82 (t, $J = 3.6$ Hz, 1 H), 7.61 (td, $J = 7.1, 0.9$ Hz, 1 H), 7.54-7.50 (m, 1 H), 7.48 (d, $J = 8.3$ Hz, 1 H), 7.45-7.40 (m, 2 H), 7.35-7.31 (m, 1 H), 6.93 (s, 1 H), 6.44 (d, $J = 10.6$ Hz, 1 H), 6.23 (d, $J = 10.6$ Hz, 1 H), 3.39 (s, 3 H); **13C NMR** (CDCl_3 , 100 MHz, ppm) δ 157.6, 151.6, 144.9, 140.8, 137.4, 136.6, 136.2, 131.7, 131.2, 130.1, 130.0, 129.6, 127.7, 127.4, 127.0, 126.8, 126.4, 126.1, 125.0, 123.2, 123.0, 122.6, 122.4, 122.2, 120.5, 120.0, 113.3, 112.2, 75.1, 56.1; **HRMS**: calculated for $\text{C}_{30}\text{H}_{21}\text{N}_3\text{NaO}_2$ [$\text{M}+\text{Na}^+$]: 478.1531; **found**: 478.1547.



$R_f = 0.45$, 50 % EtOAc in hexanes

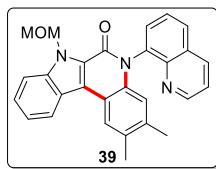
Prepared according to general procedure II. Purification of the crude product by flash column chromatography afforded the annulation product **37** as white solid in 63% yield (57 mg). **1H NMR** (CDCl_3 , 400 MHz, ppm): δ 8.80 (dd, $J = 4.2, 1.6$ Hz, 1 H), 8.41 (d, $J = 8.2$ Hz, 1 H), 8.28 (dd, $J = 8.4, 1.9$ Hz, 1 H), 8.05 (dd, $J = 7.9, 1.8$ Hz, 1 H), 7.98 (s, 1 H), 7.81 (dd, $J = 7.2, 1.8$ Hz, 1 H), 7.77 (t, $J = 7.5$ Hz, 2 H), 7.59-7.55 (m, 1 H), 7.45-7.43 (m, 1 H), 7.41 (d, $J = 8.2$ Hz, 1 H), 6.40 (d, $J = 10.8$ Hz, 1 H), 6.20 (d, $J = 10.6$ Hz, 1 H), 6.07 (s, 1 H), 5.94 (dd, $J = 13.6, 1.3$ Hz, 2 H), 3.35 (s, 3 H); **13C NMR** (CDCl_3 , 100 MHz, ppm) δ 156.6, 151.7, 147.2, 144.6, 144.1, 140.9, 136.5, 136.4, 134.2, 130.9, 130.0, 129.8, 126.9, 126.8, 125.4, 122.7,

122.6, 122.2, 121.81, 121.78, 113.2, 112.0, 102.5, 101.6, 98.2, 74.9, 55.9; **HRMS**: calculated for C₂₇H₁₉N₃NaO₄ [M+Na⁺]: 472.1273; **found**: 472.1290.



R_f = 0.45, 50 % EtOAc in hexanes

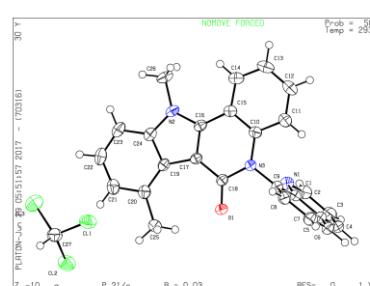
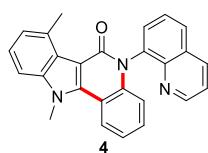
Prepared according to general procedure II. Purification of the crude product by flash column chromatography afforded the annulation product **38** as white solid in 56% yield (53 mg). **¹H NMR** (CDCl₃, 400 MHz, ppm): δ 8.79 (dd, J = 4.2, 1.6 Hz, 1 H), 8.41 (d, J = 8.2, 1 H), 8.28 (dd, J = 8.32, 1.6 Hz, 1 H), 8.06 (dd, J = 8.2, 1.4 Hz, 1 H), 7.97 (s, 1 H), 7.86 (dd, J = 7.2, 1.4 Hz, 1 H), 7.81-7.76 (m, 2 H), 7.59-7.55 (m, 1 H), 7.45-7.40 (m, 2 H), 6.41 (d, J = 10.5 Hz, 1 H), 6.21 (d, J = 10.6 Hz, 1 H), 6.07 (s, 1 H), 4.09 (s, 3 H), 3.44 (s, 3 H), 3.35 (s, 3 H); **¹³C NMR** (CDCl₃, 100 MHz, ppm) δ 156.7, 151.6, 148.6, 145.8, 144.6, 140.9, 136.5, 136.2, 133.2, 131.0, 129.8, 129.7, 126.8, 126.7, 125.5, 122.6, 122.5, 122.2, 121.7, 121.4, 112.3, 112.0, 105.7, 100.6, 74.9, 56.5, 55.9, 55.8; **HRMS**: calculated for C₂₈H₂₃N₃NaO₄ [M+Na⁺]: 488.1586; **found**: 488.1602.



R_f = 0.45, 50 % EtOAc in hexanes

Prepared according to general procedure II. Purification of the crude product by flash column chromatography afforded the annulation product **39** as white solid in 65% yield (57 mg). **¹H NMR** (CDCl₃, 400 MHz, ppm): δ 8.78 (dd, J = 4.2, 1.6 Hz, 1 H), 8.53 (d, J = 8.2 Hz, 1 H), 8.33 (s, 1 H), 8.29 (dd, J = 8.4, 1.7 Hz, 1 H), 8.05 (dd, J = 7.6, 2.0 Hz, 1 H), 7.82-7.76 (m, 3 H), 7.59-7.55 (m, 1 H), 7.45-7.44 (m, 1 H), 7.42 (t, J = 4.1 Hz, 1 H), 6.43 (d, J = 10.5 Hz, 1 H), 6.35 (s, 1 H), 6.21 (d, J = 10.6 Hz, 1 H), 3.35 (s, 3 H), 2.41 (s, 3 H), 2.10 (s, 3 H); **¹³C NMR** (CDCl₃, 100 MHz, ppm) δ 157.0, 151.6, 144.9, 140.9, 136.6, 136.5, 136.3, 135.7, 131.5, 131.0, 129.9, 129.6, 126.9, 126.6, 126.1, 124.4, 123.1, 123.0, 122.1, 121.8, 121.3, 117.5, 117.1, 112.0, 75.0, 55.9, 20.4, 19.8; **HRMS**: calculated for C₂₈H₂₃N₃NaO₂ [M+Na⁺]: 456.1688; **found**: 456.1700.

6. X-ray structure of compound 4 and compound 28:



A colorless block shaped crystal of **4** (C₂₆H₁₉N₃O) was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 293(2) K, on a Bruker D8 VENTURE CMOS photon 100

diffractometer with helios mx multilayer monochrmator Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$).

Table S1. Sample and crystal data for **4**.

Identification code	4		
Empirical formula	$C_{26}H_{19}N_3O$		
Formula weight	508.81		
Temperature	293(2) K		
Wavelength	1.54178 Å		
Crystal habit	colorless block		
Crystal system	monoclinic		
Space group	P 21/c		
Unit cell dimensions	$a = 11.0528(4) \text{ \AA}$	$\alpha = 90^\circ$	
	$b = 27.2266(9) \text{ \AA}$	$\beta = 101.4370(10)^\circ$	
	$c = 7.6920(3) \text{ \AA}$	$\gamma = 90^\circ$	
Volume	2268.79(14) \AA^3		
Z	4		
Density (calculated)	1.490 g/cm ³		
Absorption coefficient	3.876 mm ⁻¹		
F(000)	968		

Table S2. Date collection and structure refinement for **4**

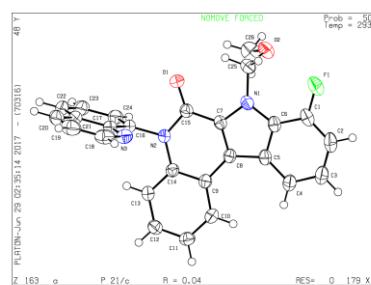
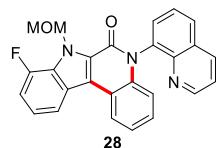
Diffractometer	CCD area detector
Radiation source	fine-focus sealed tube, CuK α
Data collection method	phi and omega scans
Theta range for data collection	3.246 to 66.541°
Index ranges	-13≤h≤13, -32≤k≤32, -8≤l≤9

Table S3. Atomic coordinates and equivalent isotropic atomic displacement parameters (\AA^2) for **4**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1)	10527(1)	841(1)	646(2)	26(1)
C(2)	9420(2)	880(1)	-2195(2)	35(1)
C(3)	10070(2)	485(1)	-2748(2)	37(1)
C(4)	10983(2)	268(1)	-1547(2)	34(1)
C(5)	11257(1)	447(1)	216(2)	28(1)
C(6)	12202(2)	252(1)	1550(2)	34(1)
C(7)	12410(2)	435(1)	3231(2)	35(1)

C(8)	11675(1)	820(1)	3677(2)	30(1)
C(9)	10757(1)	1016(1)	2420(2)	26(1)
C(10)	10329(1)	1896(1)	2675(2)	26(1)
C(11)	11471(2)	2003(1)	2239(2)	33(1)
C(12)	11818(2)	2484(1)	2069(2)	38(1)
C(13)	11048(2)	2865(1)	2323(2)	40(1)
C(14)	9923(2)	2766(1)	2752(2)	34(1)
C(15)	9533(1)	2281(1)	2941(2)	26(1)
C(16)	8376(1)	2136(1)	3395(2)	25(1)
C(17)	8055(1)	1645(1)	3563(2)	23(1)
C(18)	8861(1)	1254(1)	3242(2)	24(1)
C(19)	6841(1)	1633(1)	4009(2)	25(1)
C(20)	6025(1)	1266(1)	4410(2)	29(1)
C(21)	4912(2)	1425(1)	4787(2)	37(1)
C(22)	4585(2)	1919(1)	4806(2)	42(1)
C(23)	5366(2)	2281(1)	4454(2)	38(1)
C(24)	6492(1)	2132(1)	4065(2)	29(1)
C(25)	6299(2)	724(1)	4514(2)	35(1)
C(26)	7362(2)	2963(1)	3752(3)	39(1)
C(27)	4664(2)	824(1)	9700(2)	40(1)
Cl(1)	6231(1)	940(1)	9769(1)	46(1)
Cl(2)	4122(1)	373(1)	8086(1)	48(1)
Cl(3)	3777(1)	1361(1)	9289(1)	65(1)
N(1)	9606(1)	1056(1)	-566(2)	30(1)
N(2)	7431(1)	2429(1)	3706(2)	28(1)
N(3)	9989(1)	1405(1)	2865(2)	25(1)
O(1)	8644(1)	811(1)	3290(2)	30(1)
H(2)	8813	1029	-3042	42
H(3)	9880	374	-3914	44
H(4)	11422	4	-1881	41
H(6)	12688	-4	1275	41
H(7)	13041	305	4090	42
H(8)	11817	941	4830	36
H(11)	11996	1749	2063	40
H(12)	12579	2552	1780	46
H(13)	11289	3189	2205	47
H(14)	9409	3025	2921	41
H(21)	4358	1191	5038	45

H(22)	3825	2004	5061	51
H(23)	5154	2612	4475	45
H(25A)	6928	658	5540	53
H(25B)	6581	623	3467	53
H(25C)	5563	547	4600	53
H(26A)	8084	3090	4524	59
H(26B)	6640	3060	4183	59
H(26C)	7316	3091	2578	59
H(27)	4578	695	10860	48



A colorless block shaped crystal of **28** ($C_{26}H_{18}FN_3O_2$) was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 293(2) K, on a Bruker D8 VENTURE CMOS photon 100 diffractometer with helios mx multilayer monochrmator Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$).

Table S1. Sample and crystal data for **28**.

Identification code	28		
Empirical formula	$C_{26}H_{18}FN_3O_2$		
Formula weight	423.43		
Temperature	293(2) K		
Wavelength	1.54178 \AA		
Crystal habit	colorless block		
Crystal system	monoclinic		
Space group	P 21/c		
Unit cell dimensions	$a = 18.9157(7) \text{ \AA}$	$\alpha = 90^\circ$	
	$b = 8.9179(4) \text{ \AA}$	$\beta = 100.847(2)^\circ$	
	$c = 11.8376(5) \text{ \AA}$	$\gamma = 90^\circ$	
Volume	$1961.19(14) \text{ \AA}^3$		
Z	4		
Density (calculated)	1.434 g/cm 3		
Absorption coefficient	0.811 mm $^{-1}$		

F(000)	912
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Table S2. Date collection and structure refinement for **28**

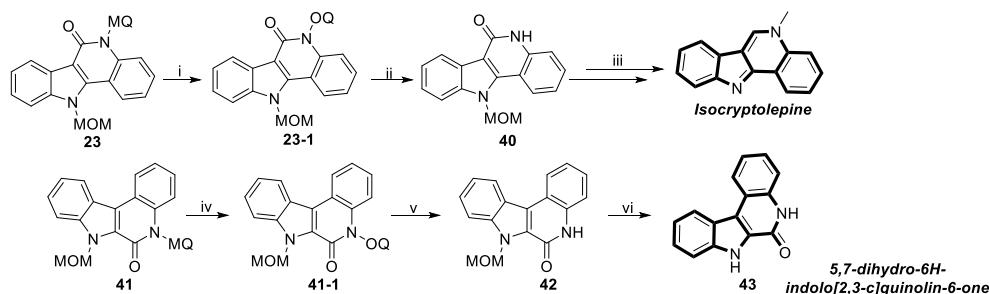
Diffractometer	CCD area detector
Radiation source	fine-focus sealed tube, CuK/ α
Data collection method	phi and omega scans
Theta range for data collection	4.76 to 66.51°
Index ranges	-19≤h≤22, -10≤k≤10, -14≤l≤13

Table S3. Atomic coordinates and equivalent isotropic atomic displacement parameters (\AA^2) for **28**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C1 C	0.09260(8)	0.82260(19)	-0.18524(12)	0.0381(3)
C2 C	0.06850(9)	0.6845(2)	-0.22310(13)	0.0454(4)
C3 C	0.08710(9)	0.5585(2)	-0.15303(14)	0.0444(4)
C4 C	0.13060(8)	0.57110(18)	-0.04624(13)	0.0381(3)
C5 C	0.15653(7)	0.71332(17)	-0.00733(11)	0.0317(3)
C6 C	0.13562(7)	0.84078(17)	-0.07600(12)	0.0334(3)
C7 C	0.20402(7)	0.92280(16)	0.08593(11)	0.0295(3)
C8 C	0.20247(7)	0.76866(16)	0.09557(11)	0.0291(3)
C9 C	0.24393(7)	0.69523(16)	0.19494(11)	0.0291(3)
C10 C	0.24947(8)	0.53925(16)	0.21101(12)	0.0329(3)
C11 C	0.28973(8)	0.47737(17)	0.30878(13)	0.0365(3)
C12 C	0.32417(8)	0.57081(17)	0.39671(13)	0.0373(3)
C13 C	0.32036(8)	0.72419(17)	0.38312(12)	0.0342(3)
C14 C	0.28241(7)	0.78786(15)	0.28175(12)	0.0292(3)
C15 C	0.24426(7)	1.02075(16)	0.17261(12)	0.0311(3)
C16 C	0.33039(7)	1.03426(15)	0.34838(11)	0.0298(3)
C17 C	0.40139(8)	1.05689(15)	0.32782(12)	0.0314(3)
C18 C	0.48818(9)	1.01839(19)	0.22031(16)	0.0479(4)
C19 C	0.53903(9)	1.1040(2)	0.29365(19)	0.0554(5)
C20 C	0.51922(9)	1.16736(19)	0.38672(17)	0.0511(4)
C21 C	0.44917(8)	1.14477(16)	0.40884(13)	0.0377(3)
C22 C	0.42540(10)	1.20441(18)	0.50545(14)	0.0458(4)
C23 C	0.35713(10)	1.17957(18)	0.52257(13)	0.0442(4)
C24 C	0.30931(8)	1.09379(17)	0.44243(12)	0.0365(3)
C25 C	0.14910(8)	1.12221(17)	-0.06056(13)	0.0362(3)
C26 C	0.06242(10)	1.1862(2)	0.05293(15)	0.0523(4)

F1 F	0.07492(5)	0.94377(12)	-0.25343(8)	0.0535(3)
N1 N	0.16361(6)	0.96884(14)	-0.01895(10)	0.0329(3)
N2 N	0.28164(6)	0.94445(13)	0.26721(9)	0.0299(3)
N3 N	0.42129(7)	0.99394(14)	0.23357(11)	0.0379(3)
O1 O	0.24702(6)	1.15831(11)	0.16731(9)	0.0409(3)
O2 O	0.07815(6)	1.16764(13)	-0.05936(9)	0.0433(3)
H2 H	0.0397	0.6736	-0.2955	0.054
H3 H	0.0697	0.4647	-0.1791	0.053
H4 H	0.1427	0.4867	-0.0005	0.046
H10 H	0.2253	0.4762	0.1540	0.039
H11 H	0.2940	0.3738	0.3162	0.044
H12 H	0.3497	0.5296	0.4644	0.045
H13 H	0.3433	0.7860	0.4420	0.041
H18 H	0.5025	0.9749	0.1569	0.058
H19 H	0.5852	1.1172	0.2789	0.066
H20 H	0.5519	1.2261	0.4364	0.061
H22 H	0.4568	1.2616	0.5583	0.055
H23 H	0.3422	1.2191	0.5869	0.053
H24 H	0.2626	1.0776	0.4540	0.044
H25A H	0.1821	1.1899	-0.0128	0.043
H25B H	0.1579	1.1293	-0.1385	0.043
H26A H	0.0610	1.0898	0.0885	0.079
H26B H	0.0166	1.2347	0.0474	0.079
H26C H	0.0991	1.2467	0.0985	0.079

7. Applications of Cu-mediated *ortho*-C-H/N-H annulation in the synthesis of cryptolepine alkaloids.



i) 5 equiv. BBr_3/DCM , 0.05 N in DCM, r.t., 3 h, 67% yield. ii) 3 equiv $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{AcOH:H}_2\text{O}$ (1:1), 60°C , 12 h, 65% yield. iii) ref 8

iv) 10 equiv BBr_3/DCM , 0.05 N in DCM, r.t., 5.5 h, 58% yield. v) 3.5 equiv Phl(TFA)_2 , $\text{MeCN:H}_2\text{O}$ (1:1), 2 d DMSO , 0°C , 6 h, 43% yield. vi) 1 N HCl , dioxane, 80°C , 1 h, >90 yield.

1) The synthesis of *Isocryptolepine*.

Intermediate 23-1: **23** (0.10 mmol, 43 mg) and anhydrous dichloromethane (2.0 ml) was added into a 10 mL glass vial (purged with Ar, sealed with PTFE cap). The resulting solution was cooled to 0°C , and BBr_3 (1.0 M in

dichloromethane solution, 5.0 equiv., 0.50 ml) was added under 0°C, then allowed to warm to room temperature and stirred for 3 h, which was then quenched by H₂O at 0°C. The combined organic phase was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The resulting residue was purified by silica gel flash chromatography to give the annulation product **23-1** in 67% (29 mg) isolated yield ($R_f = 0.45$, 3.33% MeOH in CHCl₃). **¹H NMR** (DMSO, 400 MHz, ppm): δ 10.97 (s, 1 H), 8.65-8.63 (m, 2 H), 8.48-8.45 (m, 1 H), 8.26 (d, $J = 7.6$ Hz, 1 H), 8.06 (d, $J = 8.4$ Hz, 1 H), 7.66 (d, $J = 8.1$ Hz, 1 H), 7.52-7.47 (m, 2 H), 7.37-7.31 (m, 3 H), 7.16 (d, $J = 7.9$ Hz, 1 H), 6.62-6.59 (m, 1 H), 6.15 (s, 2 H), 3.47 (s, 3 H); **¹³C NMR** (DMSO, 100 MHz, ppm) δ 159.3, 154.1, 151.0, 144.9, 141.2, 140.1, 139.7, 131.5, 131.3, 129.1, 126.1, 124.8, 124.0, 123.7, 122.1, 121.7, 121.0, 120.7, 120.6, 117.1, 112.7, 110.4, 108.4, 108.3, 74.9, 55.6; **HRMS**: calculated for C₂₆H₂₀N₃O₃ [M+H⁺]: 422.1499; **found**: 422.1516.

Compound 40: **23-1** (0.1 mmol, 42 mg) and AcOH (1.0 ml) were in 10 mL glass vial (purged with Ar, sealed with PTFE cap), and K₂Cr₂O₇ (3.0 equiv., 88 mg) dissolved in H₂O (1.0 ml) was sequentially added under argon protection. The reaction was stirred at 60°C for 12 h, and then quenched with H₂O. The mixture was extracted with chloroform. The combined organic phase was dried over anhydrous Na₂SO₄, concentrated under reduced pressure and purified by column chromatography ($R_f = 0.50$, 50 % EtOAc in hexanes) to afford **40** in 65% yield. Compound **40** is known compound which could be seen in reference 8. **¹H NMR** (CDCl₃, 400 MHz, ppm): δ 10.29 (s, 1 H), 8.62 (d, $J = 7.8$ Hz, 1 H), 8.41 (d, $J = 8.2$ Hz, 1 H), 7.65 (d, $J = 8.0$ Hz, 1 H), 7.56 (t, $J = 7.5$ Hz, 1 H), 7.52-7.48 (m, 2 H), 7.44 (t, $J = 7.4$ Hz, 1 H), 7.35 (t, $J = 7.7$ Hz, 1 H), 5.95 (s, 2 H), 3.51 (s, 3 H).

2) The synthesis of 5,7-dihydro-6H-indolo[2,3-c]quinolin-6-one **43**.

Compound 41: A mixture of amide **41a** (72 mg, 0.2 mmol, 1.0 equiv.), Cu(OAc)₂ (27 mg, 0.15mmol, 0.75 equiv.), TBAI (111 mg, 0.3 mmol, 1.5 equiv.), CsF (36.5 mg, 1.2 equiv.), and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (120 mg, 2 equiv.) in DMF (1.0 mL)/MeCN (1.0 mL) in a 10 mL glass vial (purged with O₂, sealed with PTFE cap) was heated at 100 °C for 1 hour. The reaction mixture was cooled to RT. The resulting residue was purified by silica gel flash chromatography to give the annulation product **41** in 63% (55 mg) isolated yield ($R_f = 0.4$, 50% EtOAc in hexanes). **¹H NMR** (CDCl₃, 400 MHz, ppm): δ 8.75 (dd, $J = 4.2$, 1.7 Hz, 1 H), 8.68 (dd, $J = 8.5$, 1.7 Hz, 1 H), 8.58 (dd, $J = 8.0$, 1.2 Hz, 1 H), 8.52 (d, $J = 8.2$ Hz, 1 H), 7.79 (d, $J = 8.4$ Hz, 1 H), 7.72 (d, $J = 8.2$ Hz, 1 H), 7.58 (td, $J = 7.2$, 0.9 Hz, 1 H), 7.46-7.42 (m, 1 H), 7.40 (dd, $J = 8.5$, 4.2 Hz, 1 H), 7.37-7.33 (m, 1 H), 7.20-7.15 (m, 1 H), 7.06 (d, $J = 8.2$ Hz, 1 H), 6.68 (dd, $J = 8.5$, 0.8 Hz, 1 H), 6.44 (d, $J = 10.6$ Hz, 1 H), 6.24 (d, $J = 10.6$ Hz, 1 H), 4.11 (s, 3 H), 3.37 (s, 3 H); **¹³C NMR** (CDCl₃, 100 MHz, ppm) δ 157.3, 156.2, 151.8, 145.2, 140.9, 138.6, 131.4, 130.9, 128.3, 126.7, 126.5, 126.4, 123.9, 123.0, 122.7, 122.2, 122.0, 121.21, 121.18, 119.3, 117.1, 112.1, 104.4, 75.0, 56.2, 56.0; **HRMS**: calculated for C₂₇H₂₂N₃O₃ [M+Na⁺]: 458.1475; **found**: 458.1479.

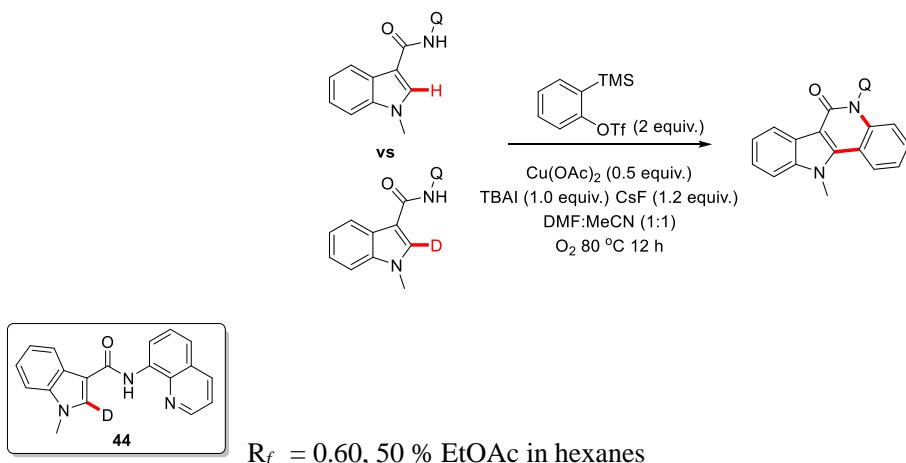
Intermediate 41-1: **41** (0.10 mmol, 43 mg) and anhydrous dichloromethane (2.0 ml) was added into a 10 mL glass vial (purged with Ar, sealed with PTFE cap). The resulting solution was cooled to 0°C, and BBr₃(1.0 M in dichloromethane solution, 10.0 equiv., 1.0 ml) was added under 0°C, then allowed to warm to room temperature and stirred for 5.5 h, which was then quenched by H₂O at 0°C. The combined organic phase was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The resulting residue was purified by silica gel flash chromatography to give the annulation product **41-1** in 58% (25 mg) isolated yield ($R_f = 0.55$, 10% MeOH in CHCl₃). **¹H NMR** (DMSO, 400 MHz, ppm): δ 11.01 (s, 1 H), 8.69-8.63 (m, 4 H), 7.91 (d, $J = 8.4$ Hz, 1 H), 7.70 (d, $J = 8.1$ Hz, 1 H), 7.65-7.61 (m, 1 H), 7.52-7.46 (m, 2 H), 7.39-7.35 (m, 1 H), 7.23 (td, $J = 8.5$, 1.2 Hz, 1 H), 7.16 (d, $J = 8.1$ Hz, 1 H), 6.56 (dd, $J = 8.4$, 0.7 Hz, 1 H), 6.24 (dd, $J = 24.6$, 10.5 Hz, 2 H),

3.21 (s, 3 H); **¹³C NMR** (DMSO, 100 MHz, ppm) δ 156.0, 154.2, 151.1, 144.7, 140.2, 138.3, 131.3, 126.7, 126.6, 125.9, 125.8, 123.6, 122.9, 122.6, 122.1, 121.8, 120.7, 119.9, 117.9, 116.7, 112.1, 108.3, 74.0, 55.3; **HRMS**: calculated for C₂₆H₂₀N₃O₃ [M+H⁺]: 422.1499; found: 422.1498.

Compound 42: 41-1 (0.1 mmol, 42 mg) and MeCN:H₂O (2 mL, 1:1 v/v) were added in flask under argon protection, and then PhI(TFA)₂ (3.5 mmol, 150 mg) and 2d DMSO was added at 0°C. The reaction was stirred at 0°C for 6 h, and then quenched with H₂O. The mixture was extracted with chloroform. The combined organic phase was dried over anhydrous Na₂SO₄, concentrated under reduced pressure and purified by column chromatography (R_f = 0.50, 33 % EtOAc in hexanes) to afford **42** in 43 % yield (12 mg). **¹H NMR** (DMSO, 400 MHz, ppm): δ 12.00 (s, 1 H), 8.58 (d, *J* = 8.1 Hz, 1 H), 8.53 (d, *J* = 7.9 Hz, 1 H), 7.85 (d, *J* = 8.1 Hz, 1 H), 7.59 (t, *J* = 7.4 Hz, 1 H), 7.52 (d, *J* = 7.7 Hz, 1 H), 7.47-7.41 (m, 2 H), 7.36 (t, *J* = 7.4 Hz, 1 H), 6.31 (s, 2 H), 3.22 (s, 3 H); **¹³C NMR** (DMSO, 100 MHz, ppm) δ 170.1, 156.0, 155.8, 135.2, 128.6, 126.7, 126.4, 126.1, 123.3, 122.7, 122.5, 121.9, 120.1, 115.9, 112.0, 73.9, 55.2; **HRMS**: calculated for C₁₇H₁₅N₂O₂ [M+H⁺]: 279.1128; **found**: 278.1130.

Compound 43: A solution of **42** (0.035 mmol, 10 mg) and 1 N HCl (0.6 mL) in 1,4-dioxane (1.3 mL) was stirred at 80 °C for 50 min. and the solution was neutralized by a saturated aqueous NaHCO₃ solution (pH=10) after cooling, and extracted with DCM. The combined organic phases were dried over Na₂SO₄ and concentrated under reduced pressure and purified by column chromatography (R_f = 0.40, 50 % EtOAc in hexanes) to afford **43** in 90 % yield. Compound **43** is known compound which could be seen in reference 9. **¹H NMR** (DMSO, 400 MHz, ppm): δ 12.35 (s, 1 H), 11.85 (s, 1 H), 8.46 (dd, *J* = 14.2, 8.3 Hz, 2 H), 7.64 (d, *J* = 8.2 Hz, 1 H), 7.48 (dd, *J* = 17.0, 8.4 Hz, 2 H), 7.41 (t, *J* = 7.2 Hz, 1 H), 7.33 (dd, *J* = 15.4, 7.9 Hz, 2 H).

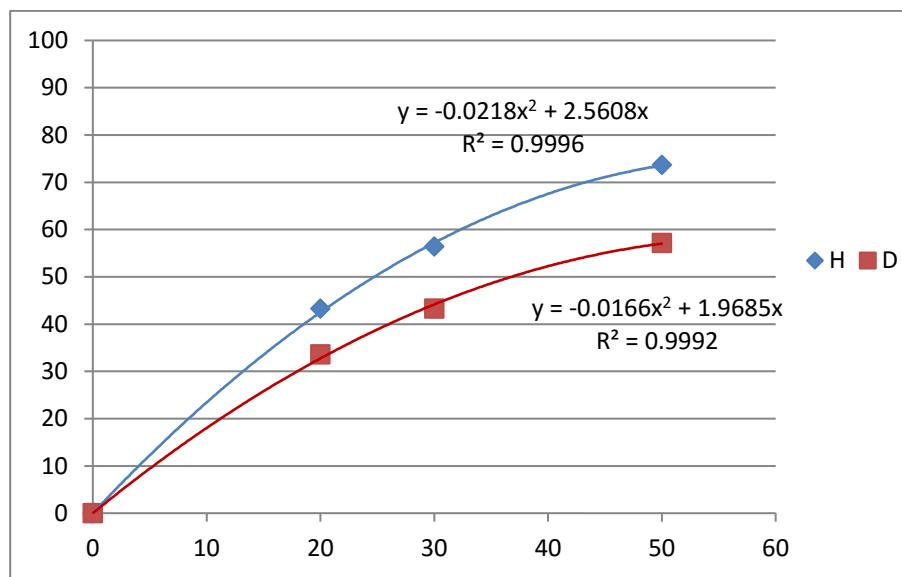
8. Preliminary mechanistic studies



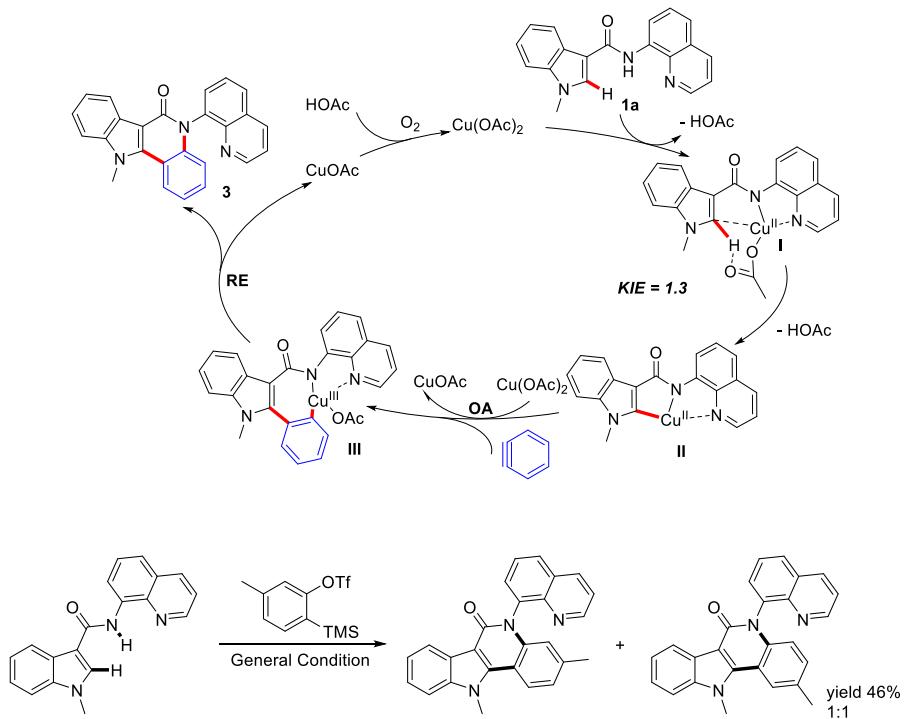
¹H NMR (CDCl₃, 400 MHz, ppm): δ 10.54 (s, 1 H), 8.96 (dd, *J* = 7.6, 1.2 Hz, 1 H), 8.89 (dd, *J* = 4.2, 1.7 Hz, 1 H), 8.47 (dd, *J* = 6.8, 1.1 Hz, 1 H), 8.17 (dd, *J* = 8.2, 1.6 Hz, 1 H), 7.91 (s, 0.2 H), 7.59 (t, *J* = 7.9 Hz, 1 H), 7.50 (dd, *J* = 8.2, 1.2 Hz, 1 H), 7.46 (dd, *J* = 8.3, 4.2 Hz, 1 H), 7.42-7.33 (m, 3 H), 3.88 (s, 3 H); **¹³C NMR** (CDCl₃, 100 MHz, ppm) δ 163.4, 148.3, 138.8, 137.5, 136.5, 135.5, 128.2, 127.7, 125.6, 122.8, 122.0, 121.7, 120.9, 120.9, 116.4, 111.8, 110.2, 33.5; **HRMS**: calculated for C₁₉H₁₅DN₃O [M+H⁺]: 303.1356; **found**: 303.1371.

Kinetic isotope effect (KIE) of the amination of substrate **1a** and **44** with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (Aryne Precursor)

Substrate **1a** or **44** was subjected to the annulation reaction with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate under the general reaction condition for 0.1-1.0 h. Data was collected at 0.2, 0.3 and 0.5 hours. Data collecting method: at specified reaction time, the reaction vial was quenched and isolated by silica gel flash chromatography. Average data of three repeating experiments were used. k_H/k_D (~1.3) was estimated based on the ratio of annulation yield.



Proposed Reaction Pathway Study



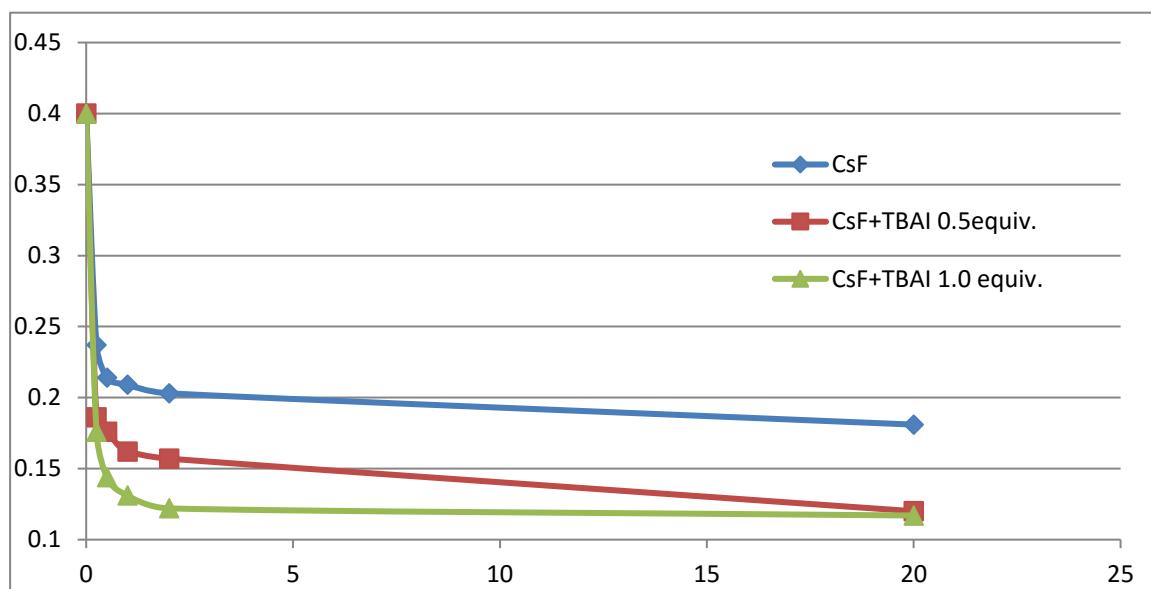
The study on generation of benzyne: A mixture of amide **1a** (60 mg, 0.2 mmol, 1 equiv.), $\text{Cu}(\text{OAc})_2$ (18.2 mg, 0.1 mmol, 0.5 equiv.), TBAI (74 mg, 0.2 mmol, 1.0 equiv.), CsF (36.5 mg, 0.24 mmol, 1.2 equiv.), and

2-(trimethylsilyl)phenyl trifluoromethanesulfonate (122 mg, 2 equiv.) in DMF (1.0 mL)/MeCN (1.0 mL) in a 10 mL glass vial (purged with O₂, sealed with PTFE cap) was heated at 80°C for 12 hours. The reaction mixture was cooled to RT. The resulting residue was purified by silica gel flash chromatography to give the annulation mix product in 60% isolated yield with ratio = 1:1.

Interval NMR Experiment on 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (Aryne Precursor) Consumption

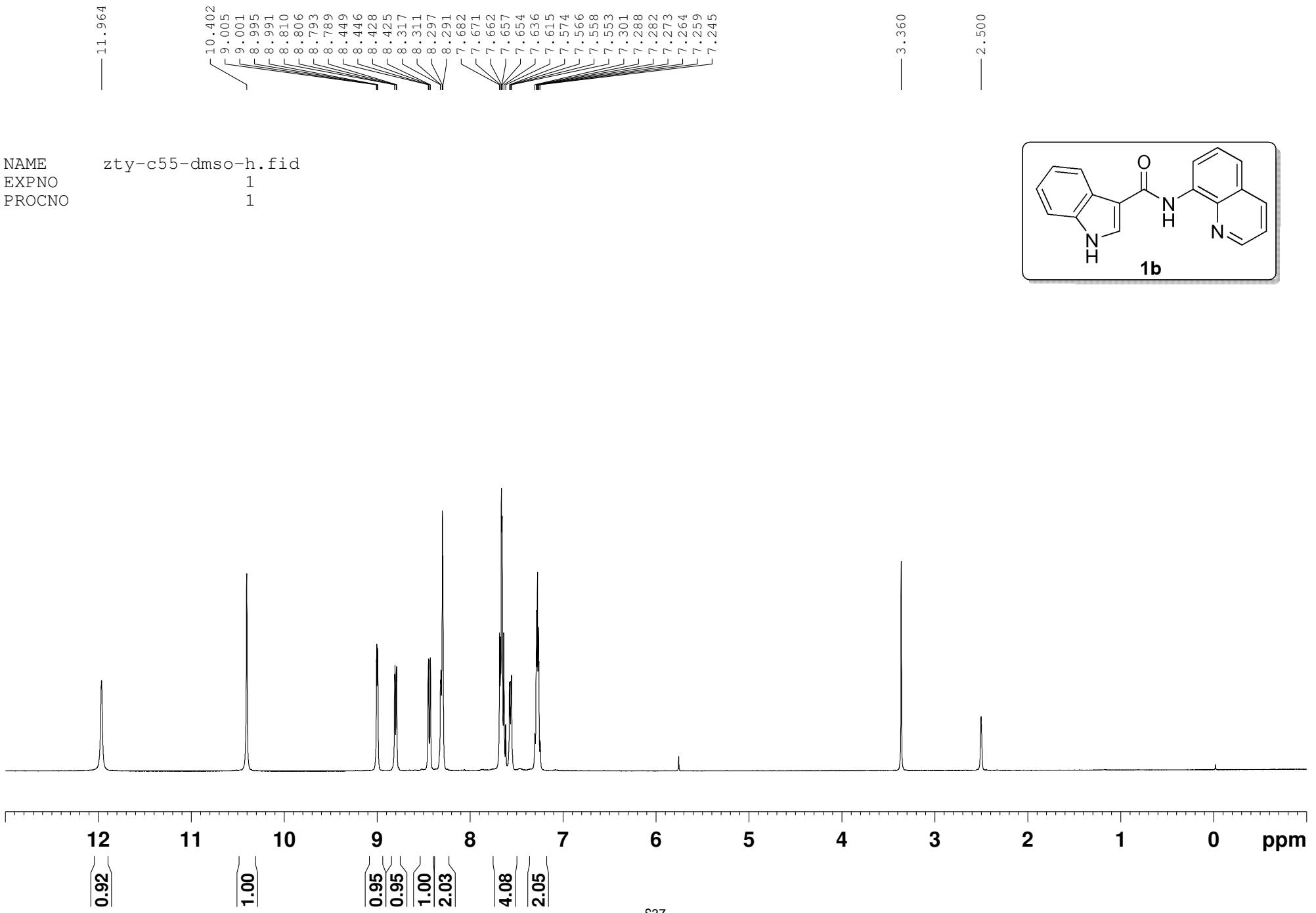
Experiment Procedure: To the solution of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.4 mmol) in MeCN/DMF (2 mL, 1:1), fluoride reagent (2.4 mmol) and additives were added. Benzotrifluoride (0.4 mmol) was also added as the internal standard. Then the reaction system was heated at 80°C, the concentration of residual aryne precursor was monitored by interval ¹⁹F-NMR experiment. The obtained data was list in the table below.

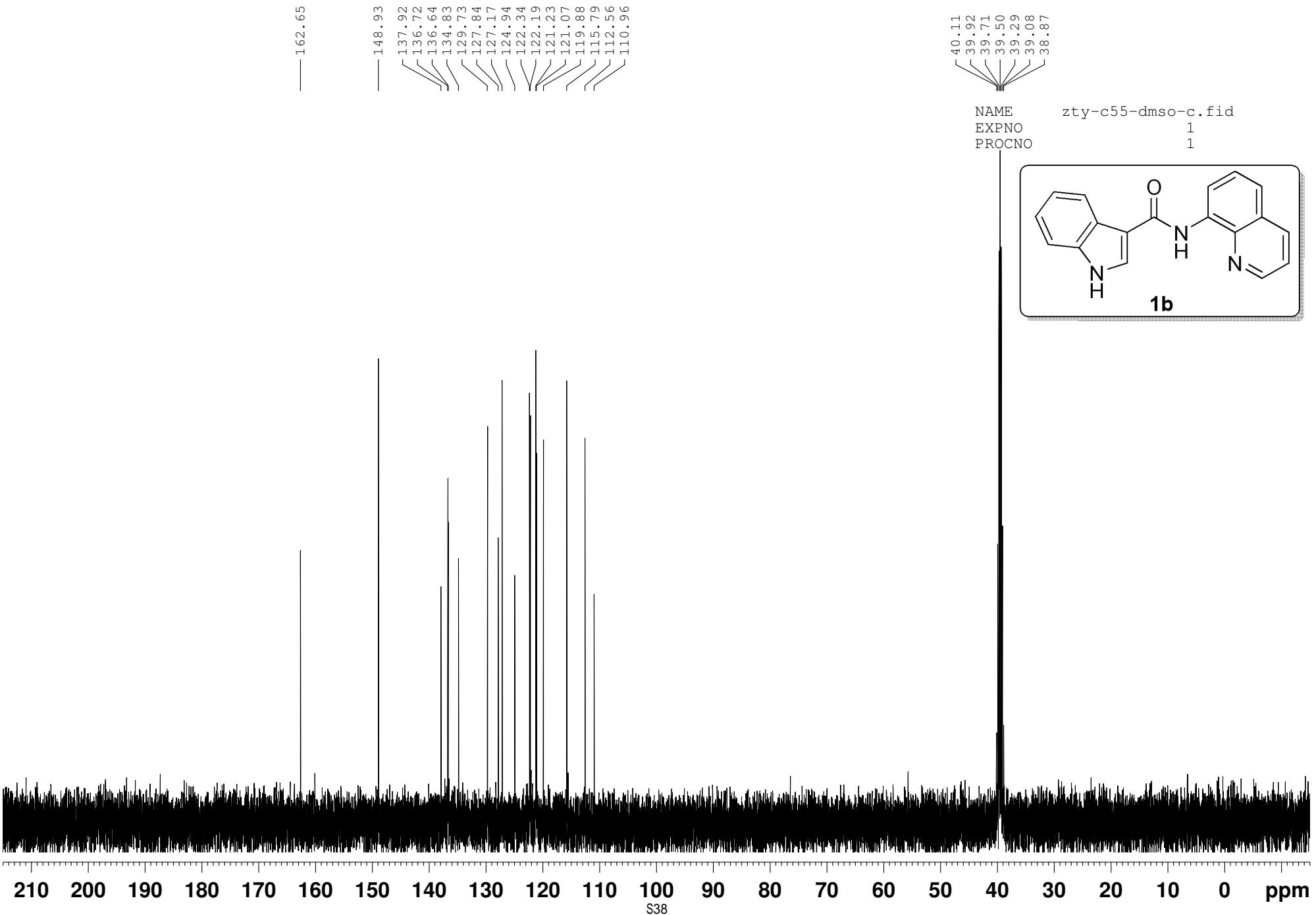
	CsF	CsF + 0.5equiv. TBAI	CsF + 1.0 equiv. TBAI
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0.25h	0.237	0.186	0.176
0.5h	0.214	0.176	0.144
1h	0.209	0.162	0.131
2h	0.203	0.157	0.122
20h	0.181	0.12	0.117

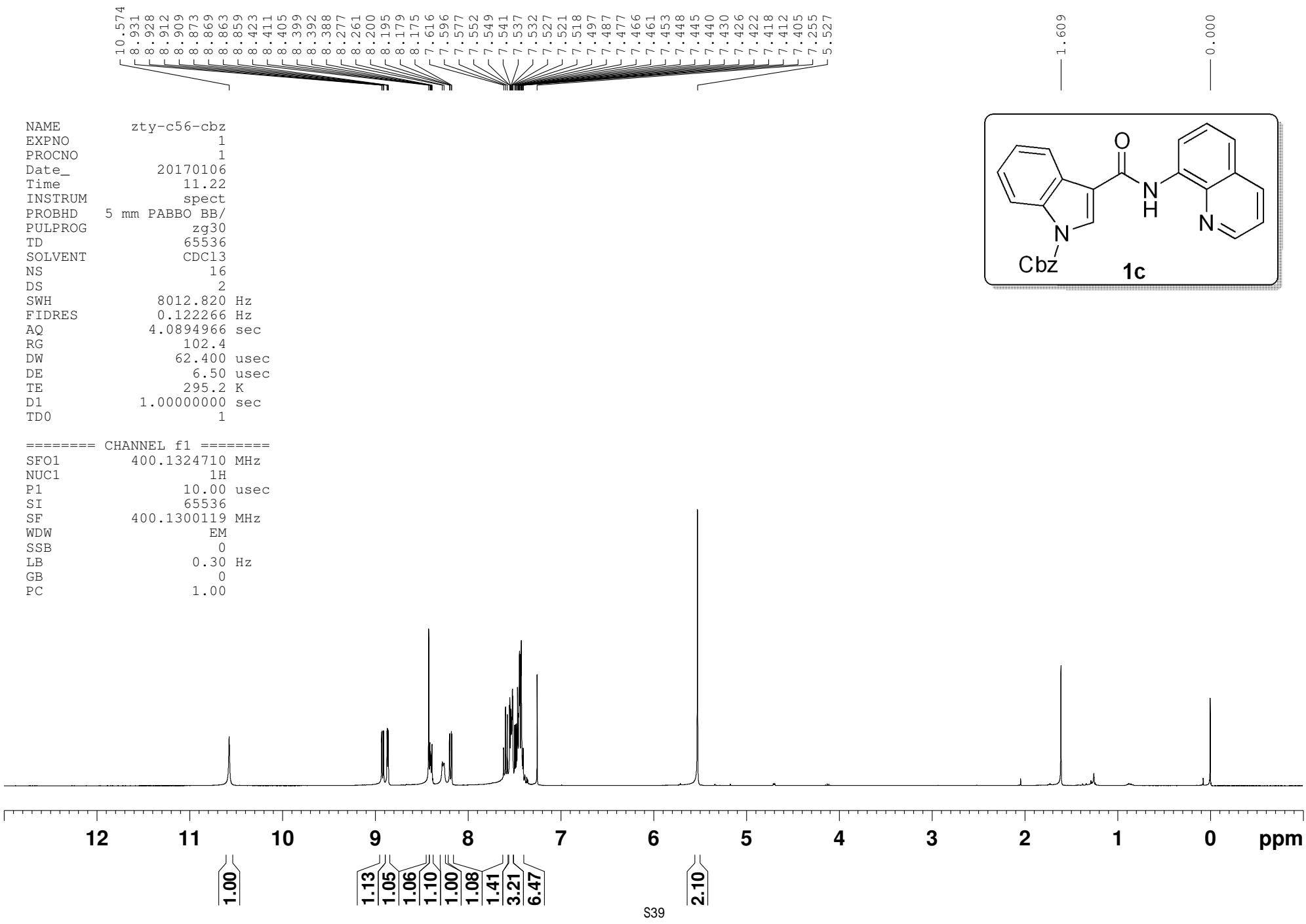


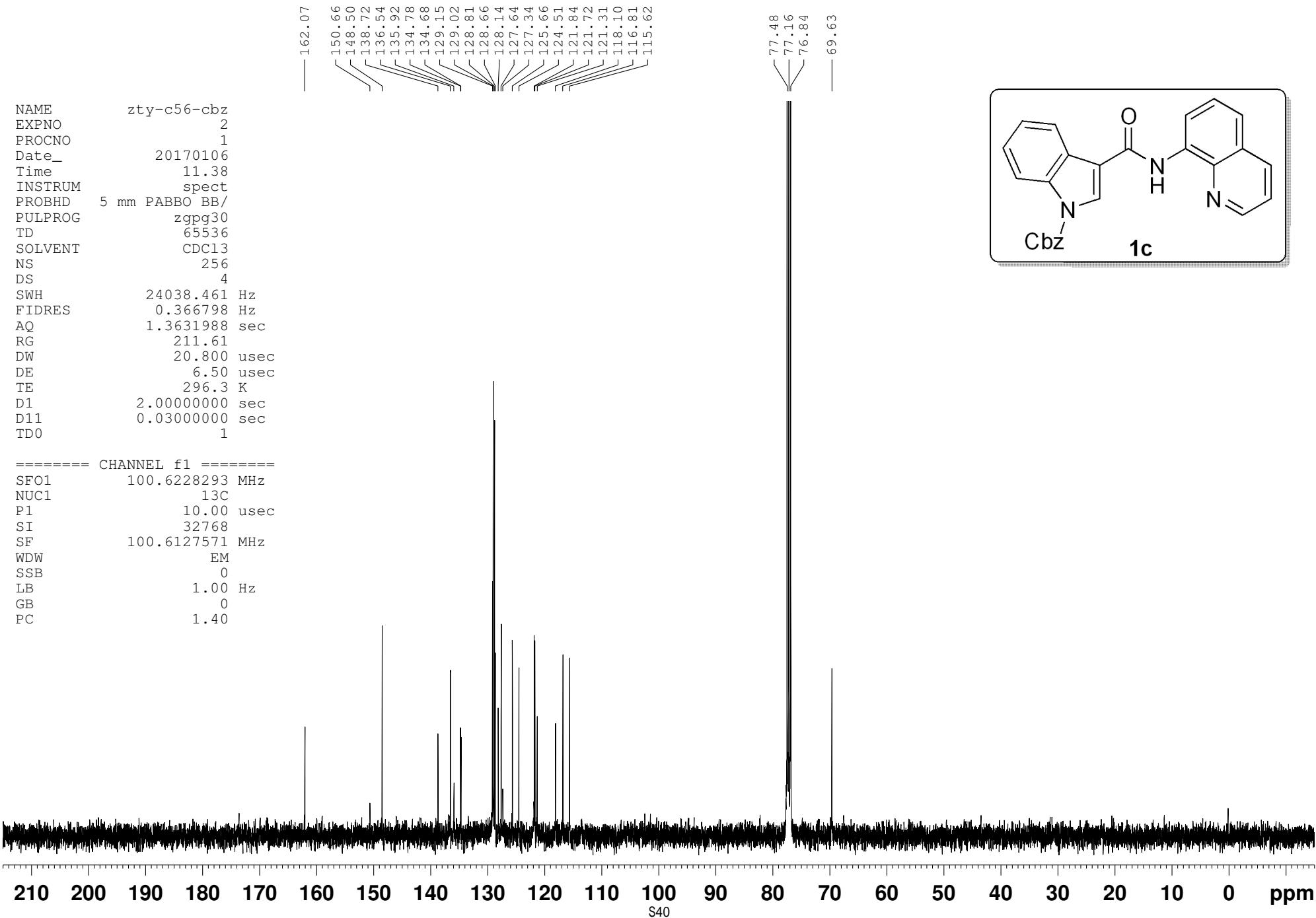
9. References:

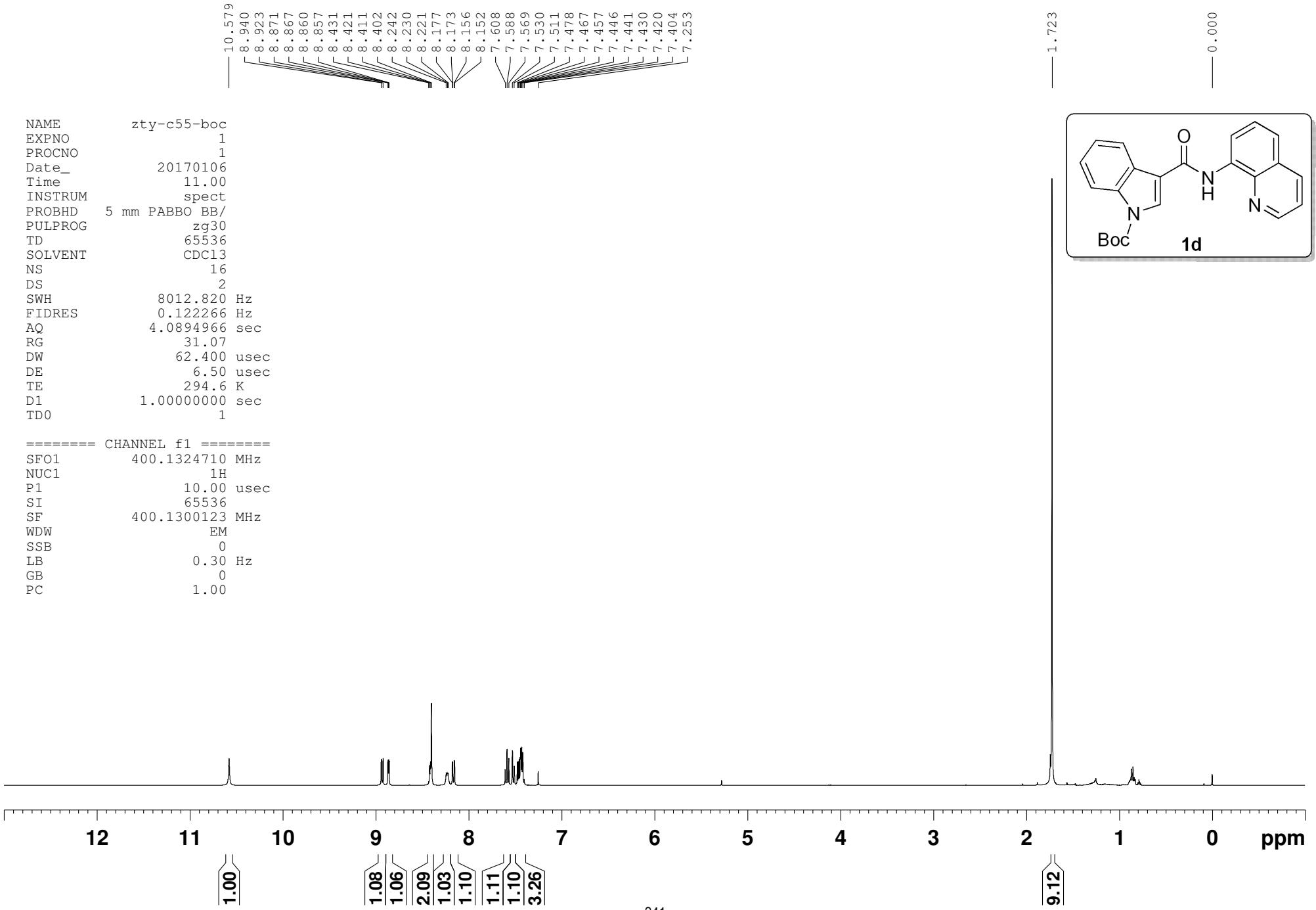
- (1) Vaillard, V. A.; Rossi, R. A.; Argüello J. E. *Org. Biomol. Chem.* **2012**, *10*, 9255.
- (2) a) Ueta, Y.; Mikami, K.; Ito, S. *Angew. Chem., Int. Ed.* **2016**, *55*, 7525. b) Shen, C.; Yang, G.; Zhang, W. *Org. Lett.* **2013**, *15*, 5722.
- (3) Truong, T.; Klimovica, K.; Daugulis, O. *J. Am. Chem. Soc.* **2013**, *135*, 9342.
- (4) Li, B.; Feng, H.-L.; Xu, S.-S.; Wang, B-Q. *Chem. Eur. J.* **2011**, *17*, 12573.
- (5) Lee, S.-H.; Mu, Y.; Kim, G.-W.; Kim, J.-S.; Park, S.-H.; Jin, T.; Lee, K.-Y.; Ham, W.-H. *Heterocycles*, **2013**, *87*, 1749.
- (6) Sauer, D. R.; Kalvin, D.; Phelan, K. M. *Org. Lett.*, **2003**, *5*, 4721.
- (7) Nishino, M.; Hirano, K.; Satoh, T.; Miura M. *Angew. Chem., Int. Ed.* **2013**, *52*, 4457.
- (8) Hayashi, K.; Choshi, T.; Chikaraishi, K.; Oda, A.; Yoshinaga, R.; Hatae, N.; Ishikura, M.; Hibino, S. *Tetrahedron*. **2012**, *68*, 4274.
- (9) Putey, A.; Popowycz, F.; Do, Q.-T.; Bernard, P.; Talapatra, S. K.; Kozielski, F.; Galmarini, C. M.; Joseph, B. *J. Med. Chem.* **2009**, *52*, 5916.

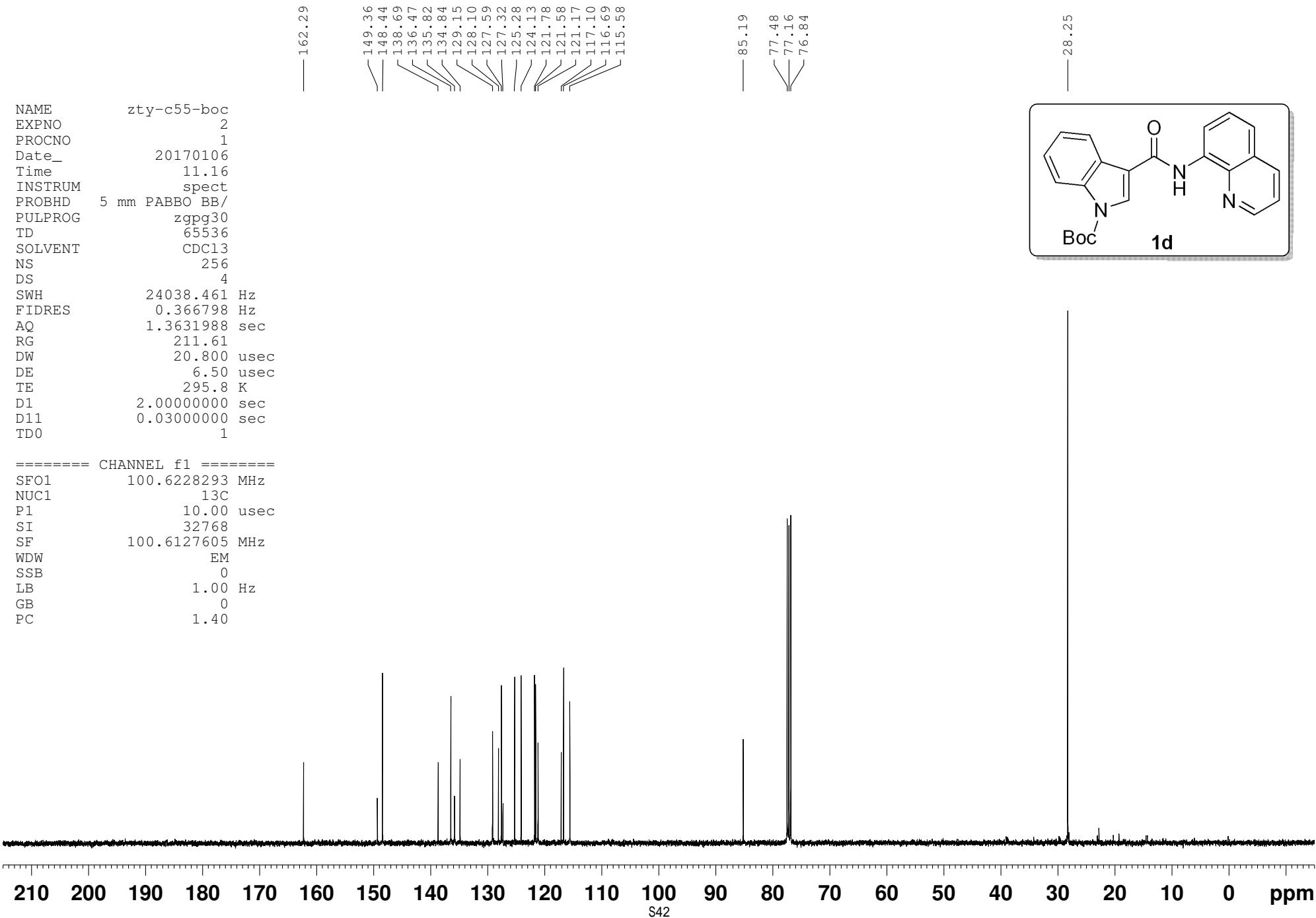


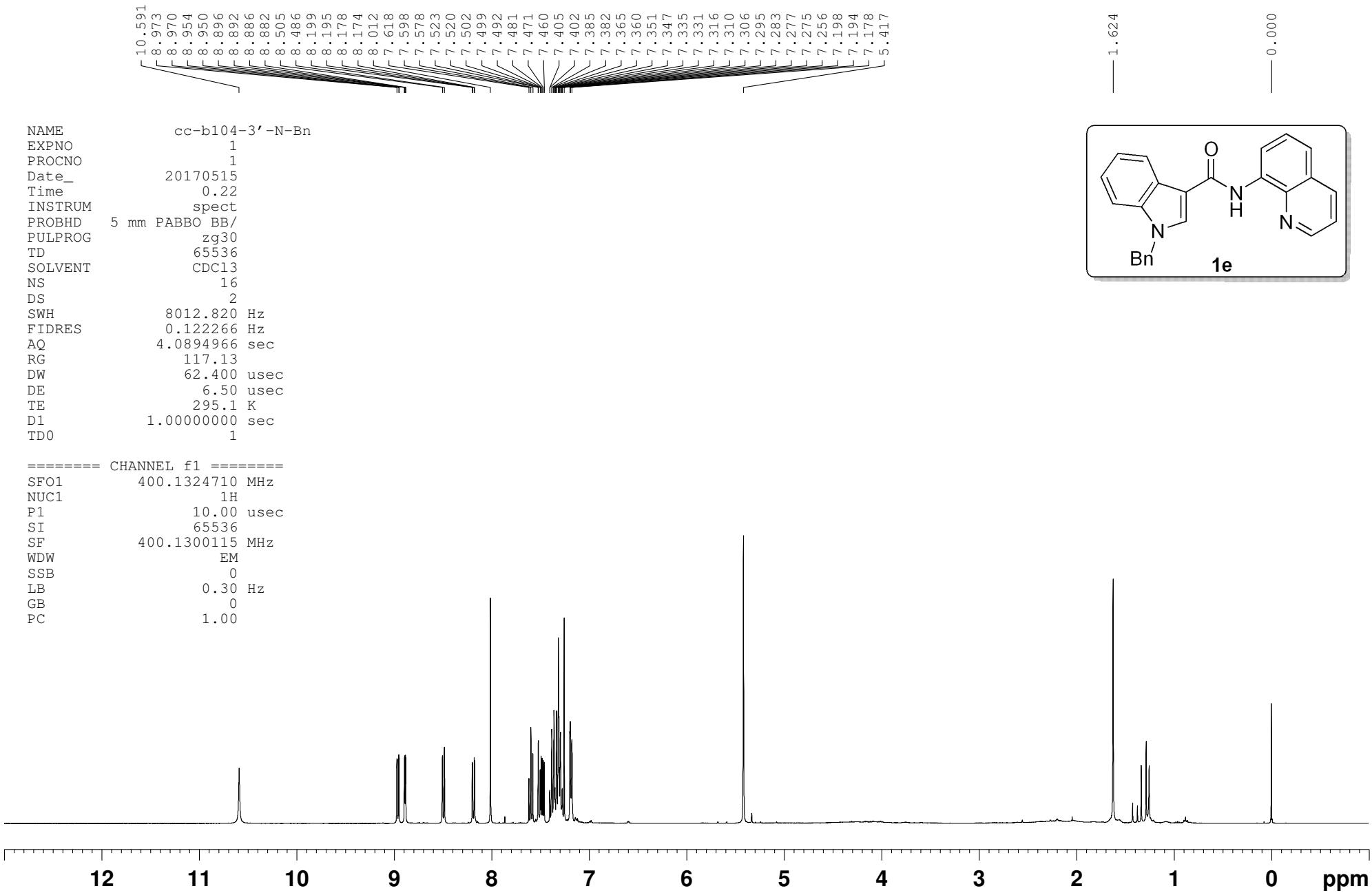


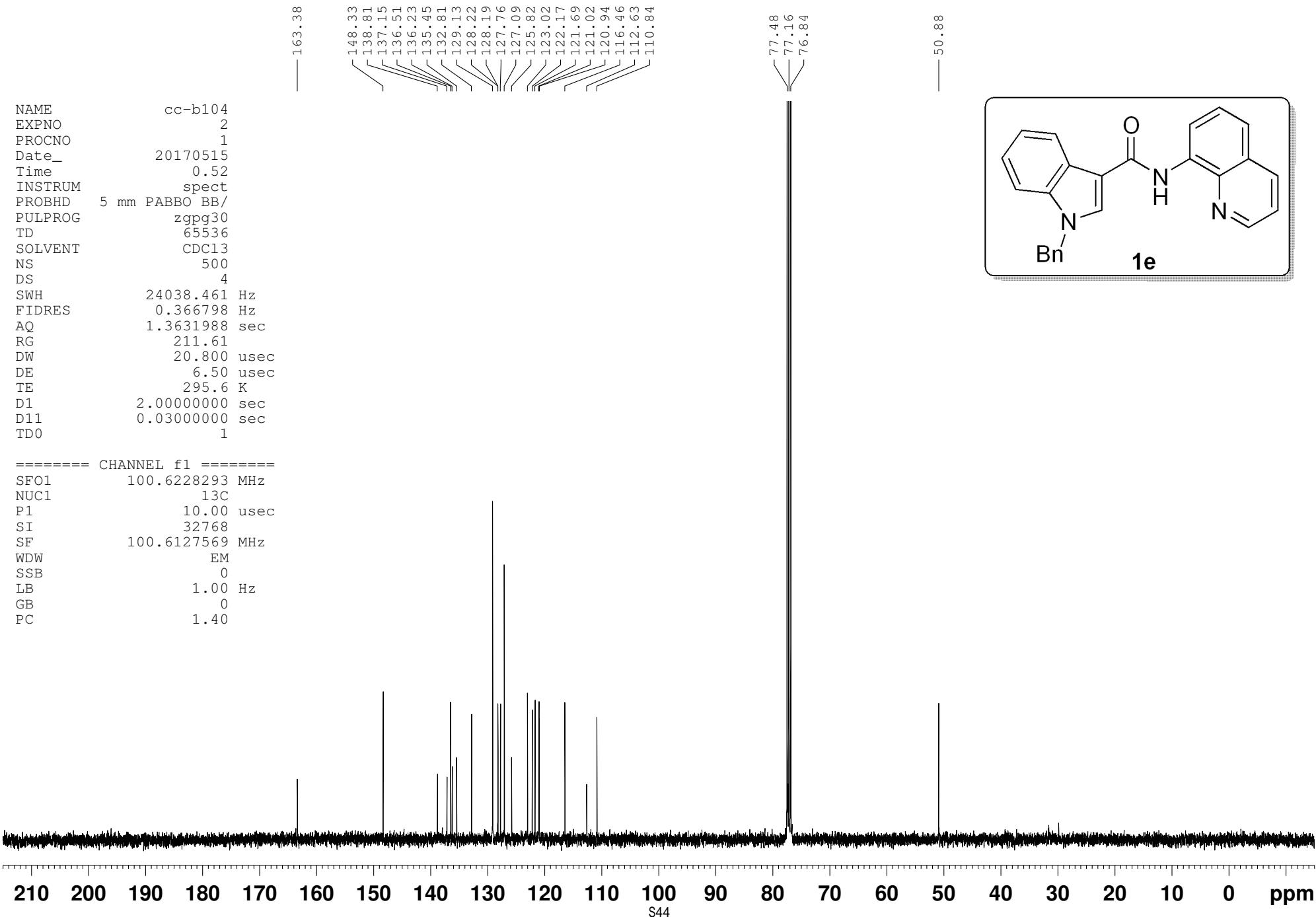


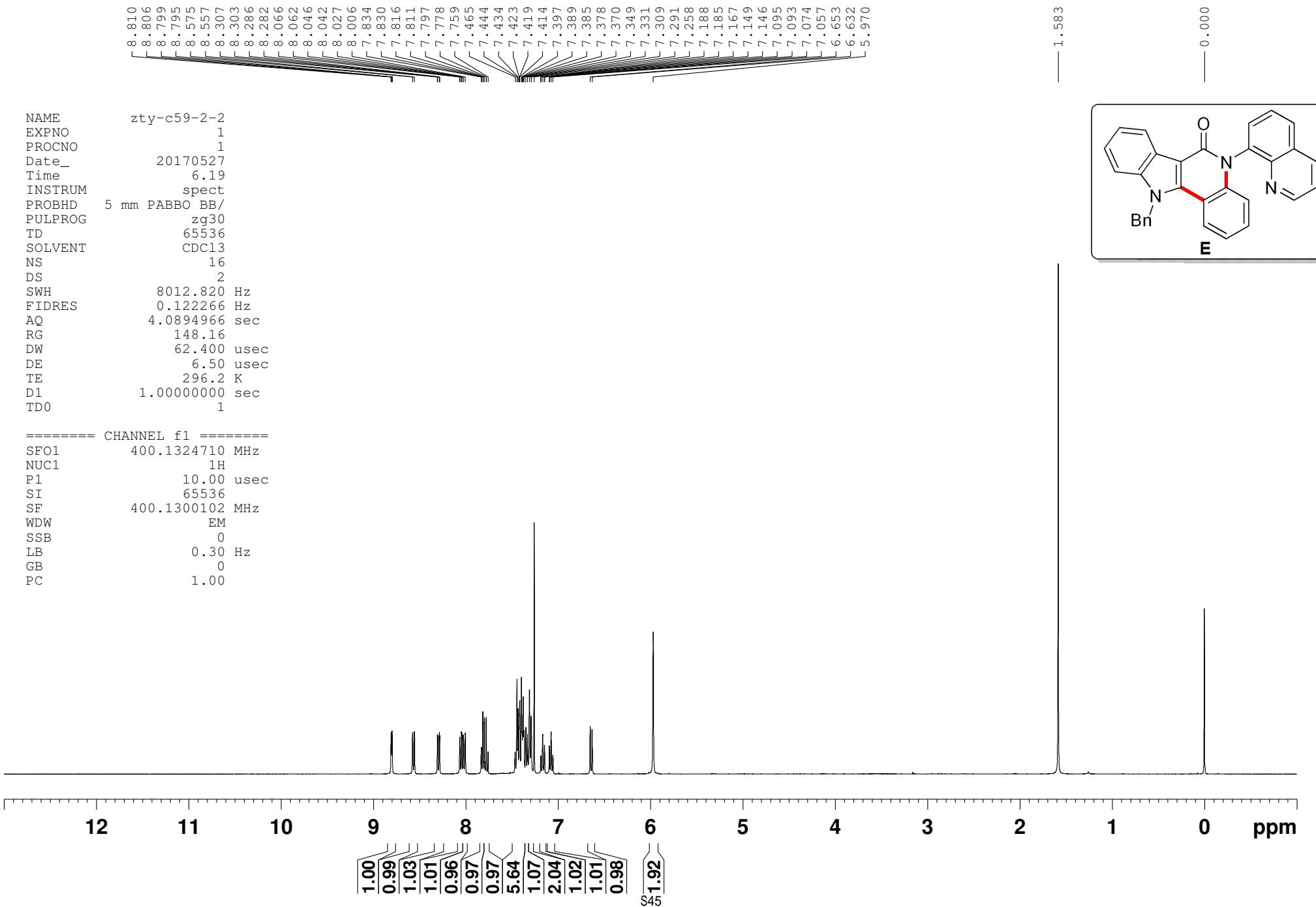


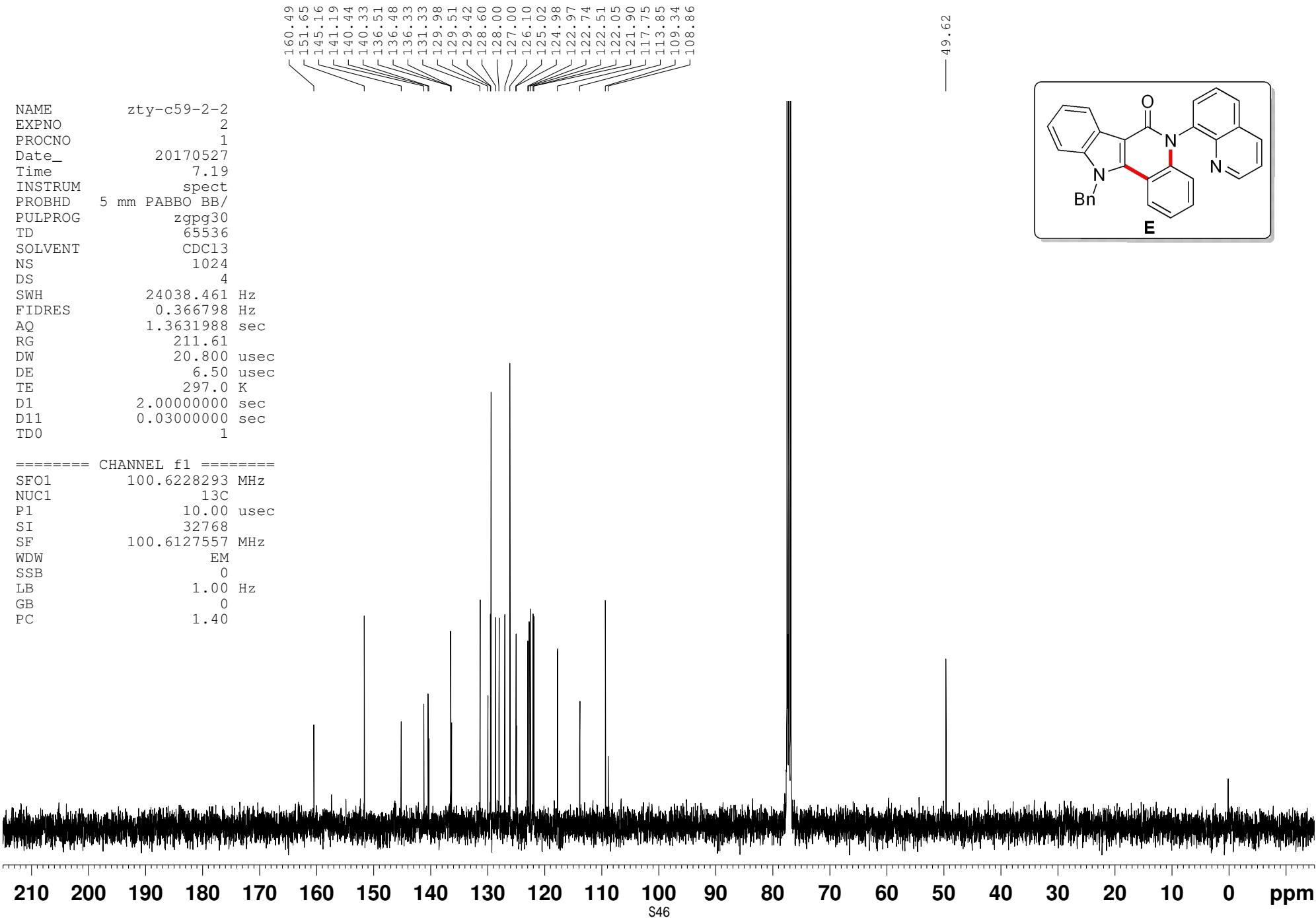


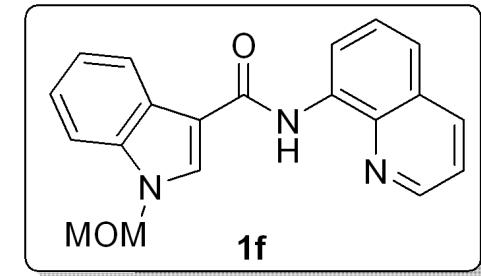
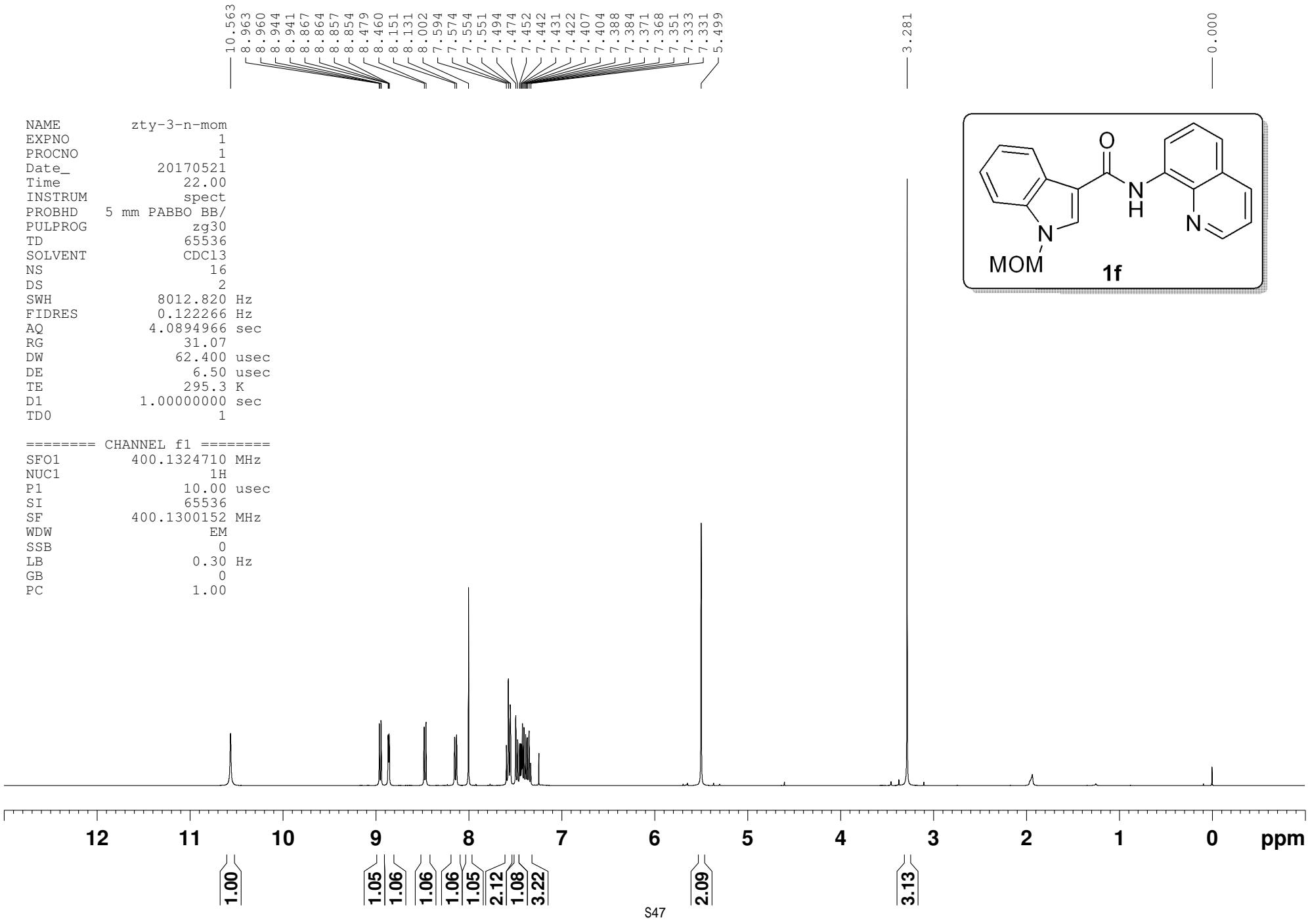


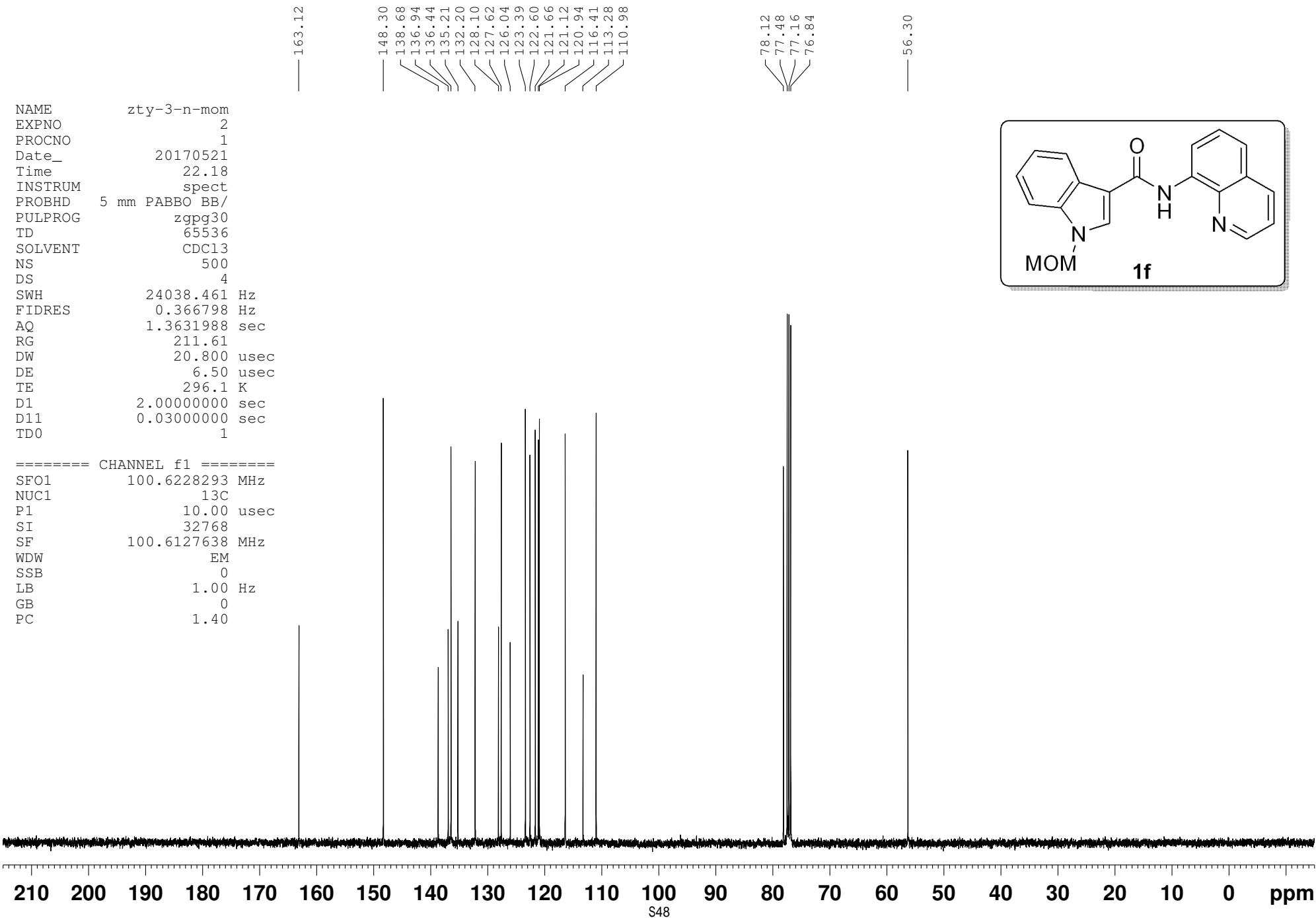


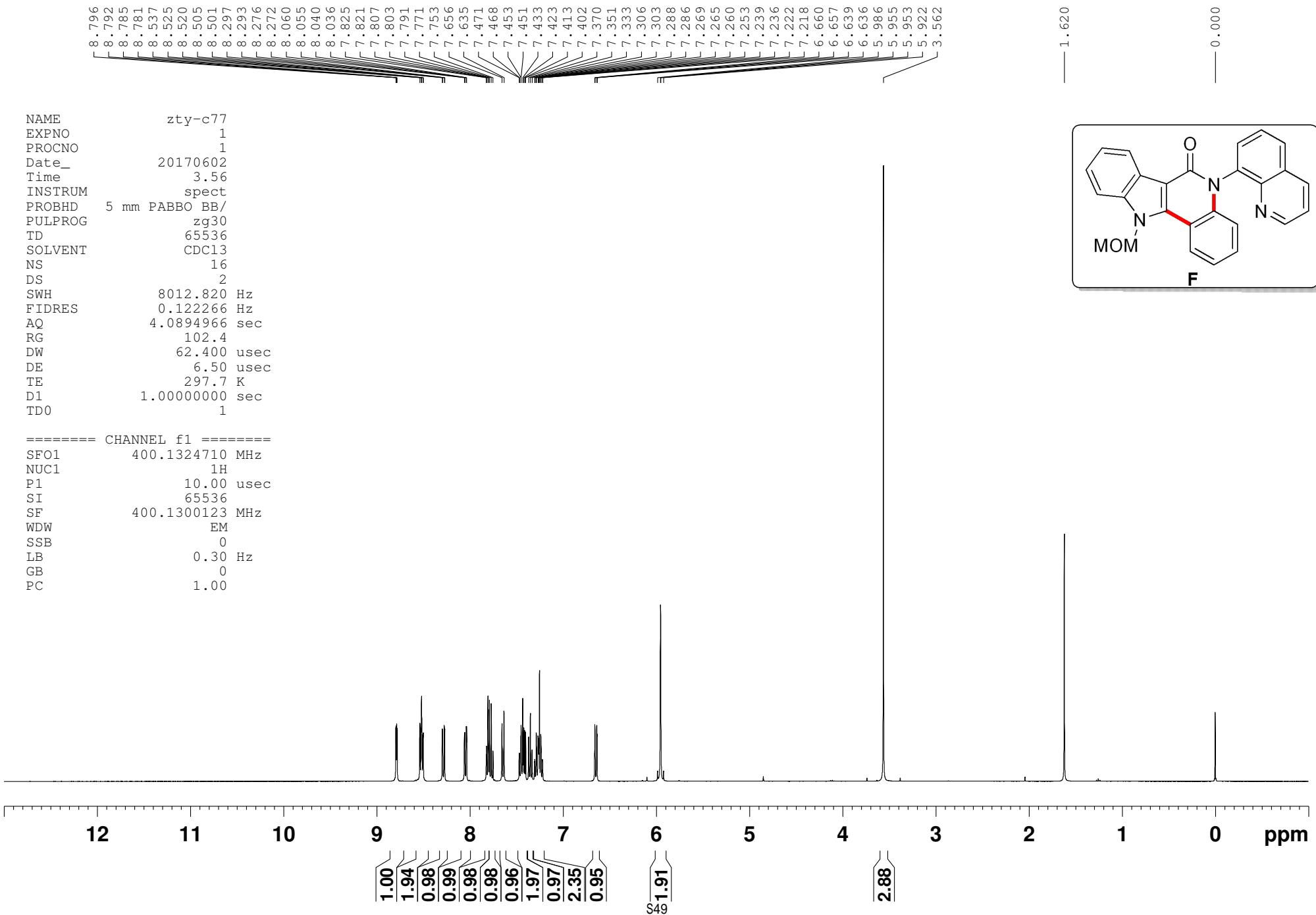










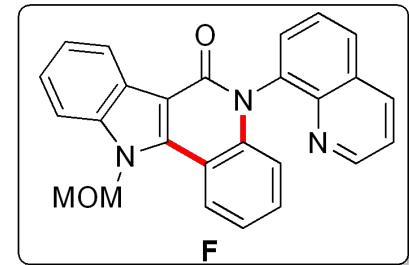
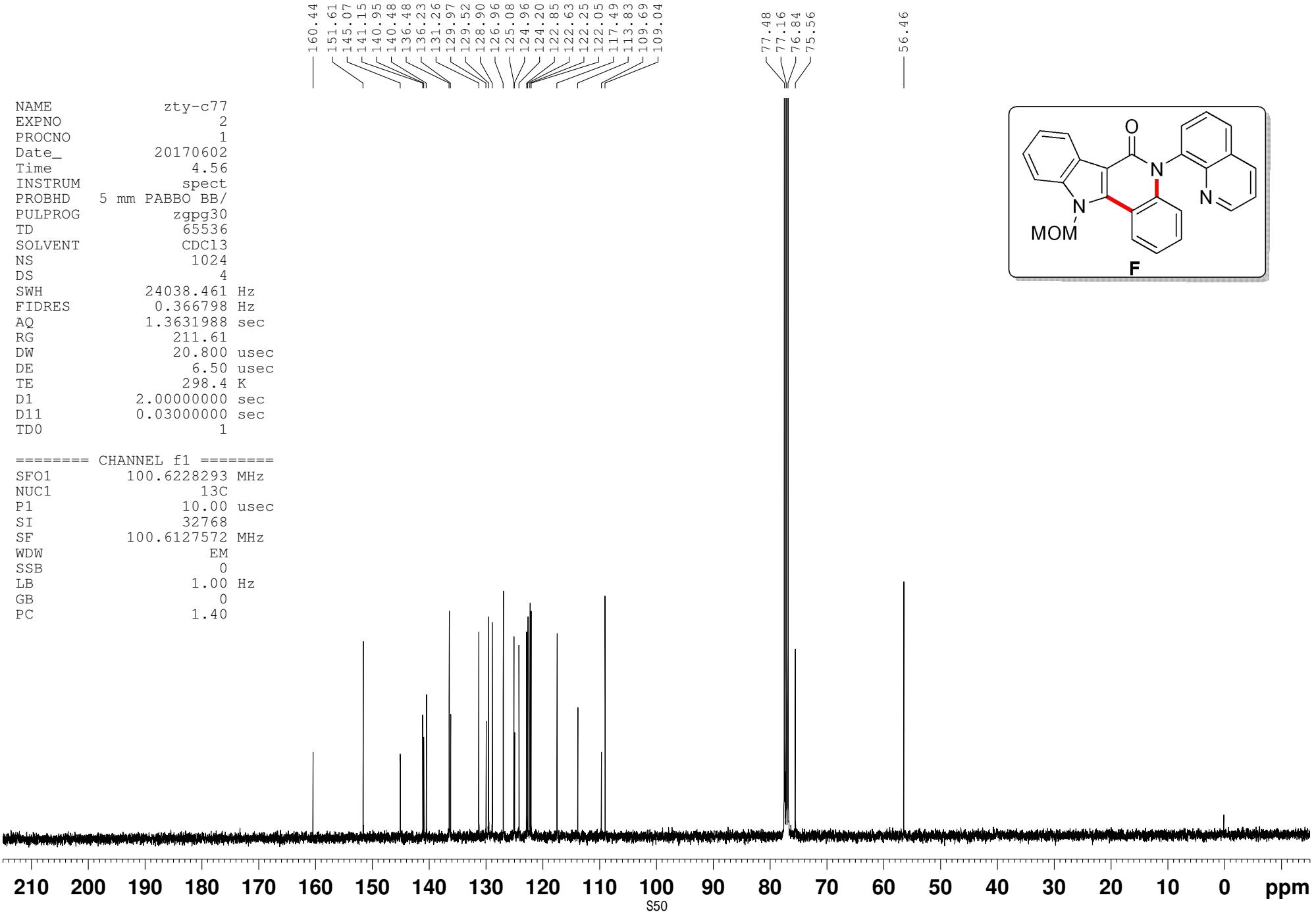


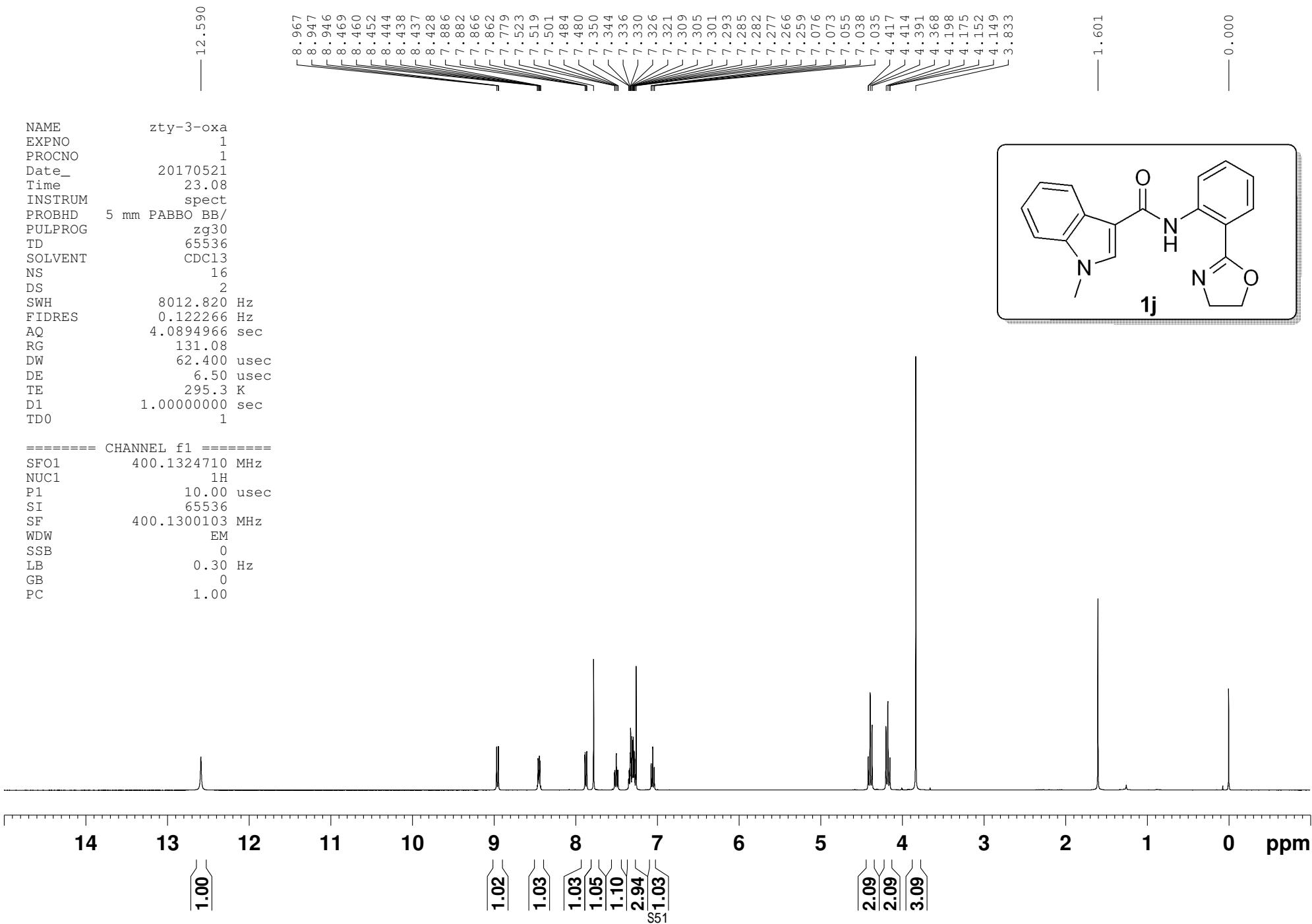
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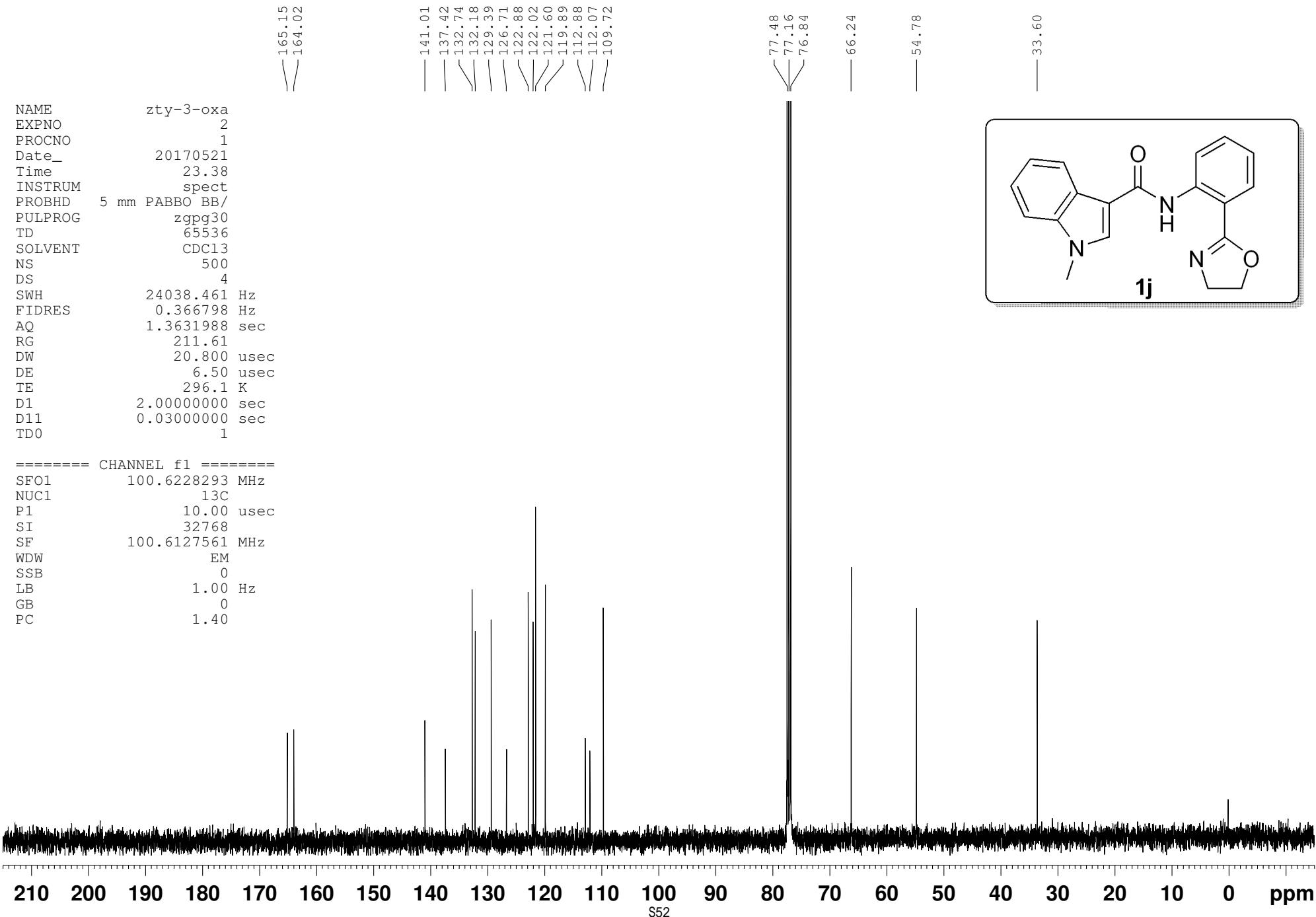
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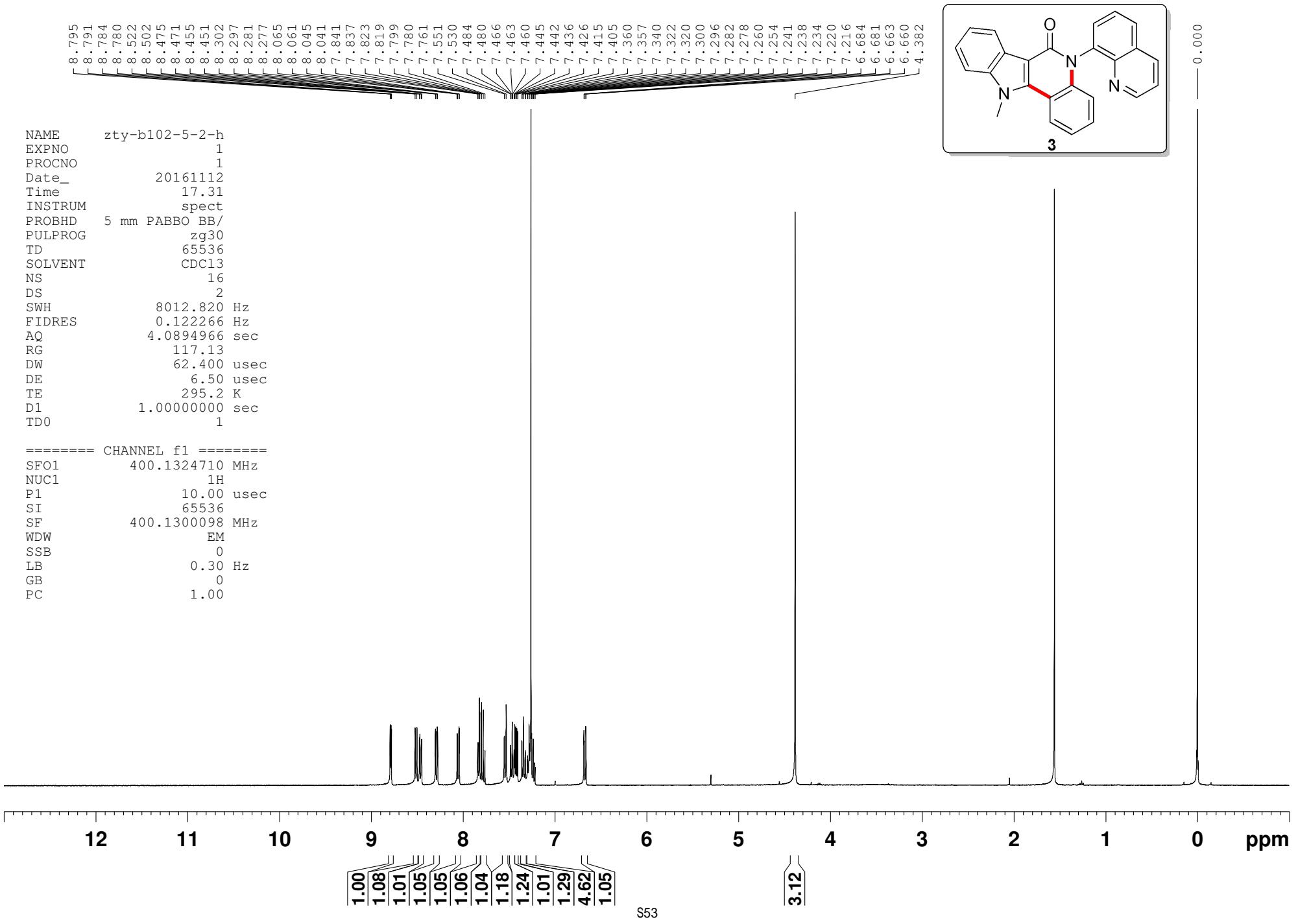
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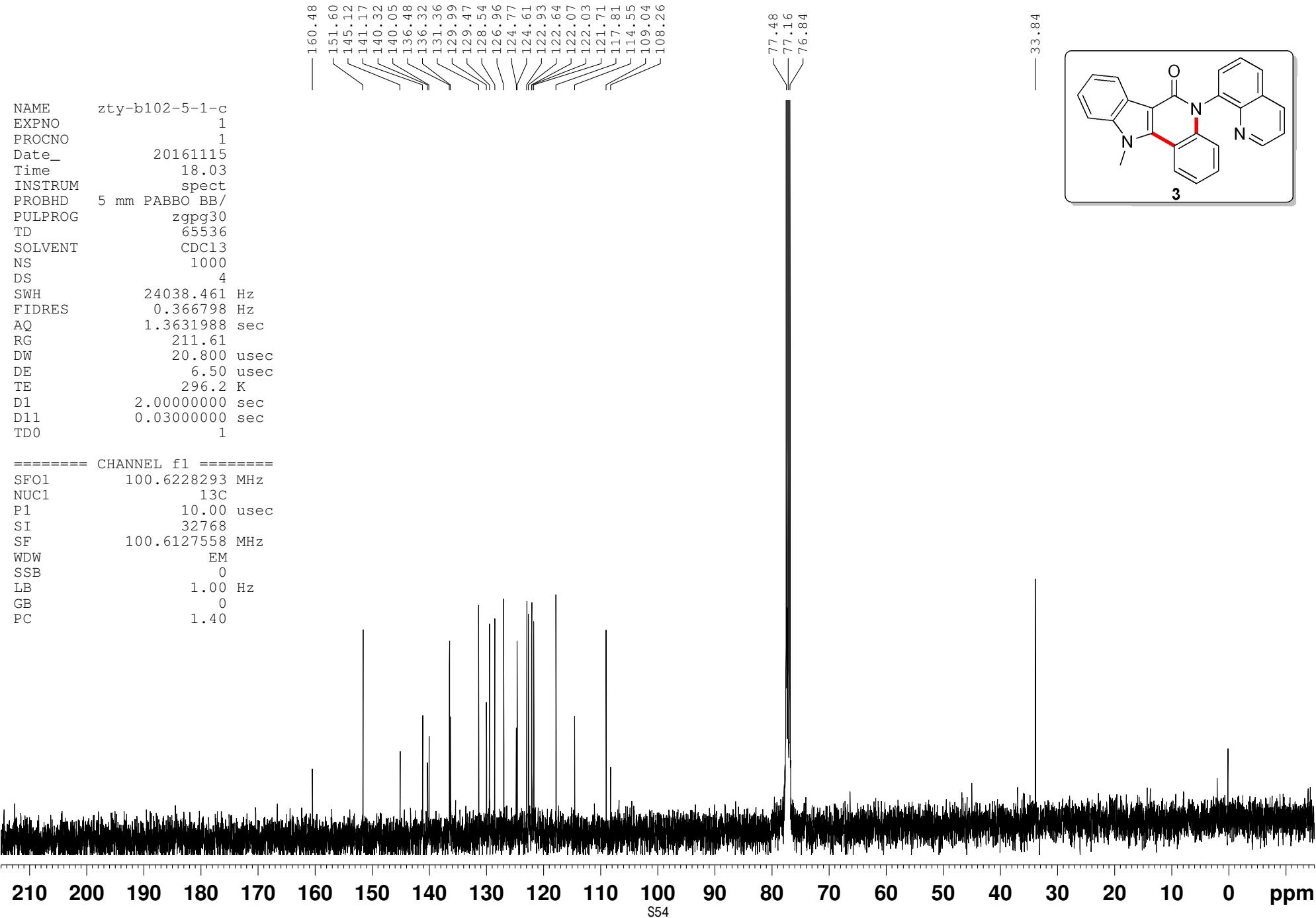


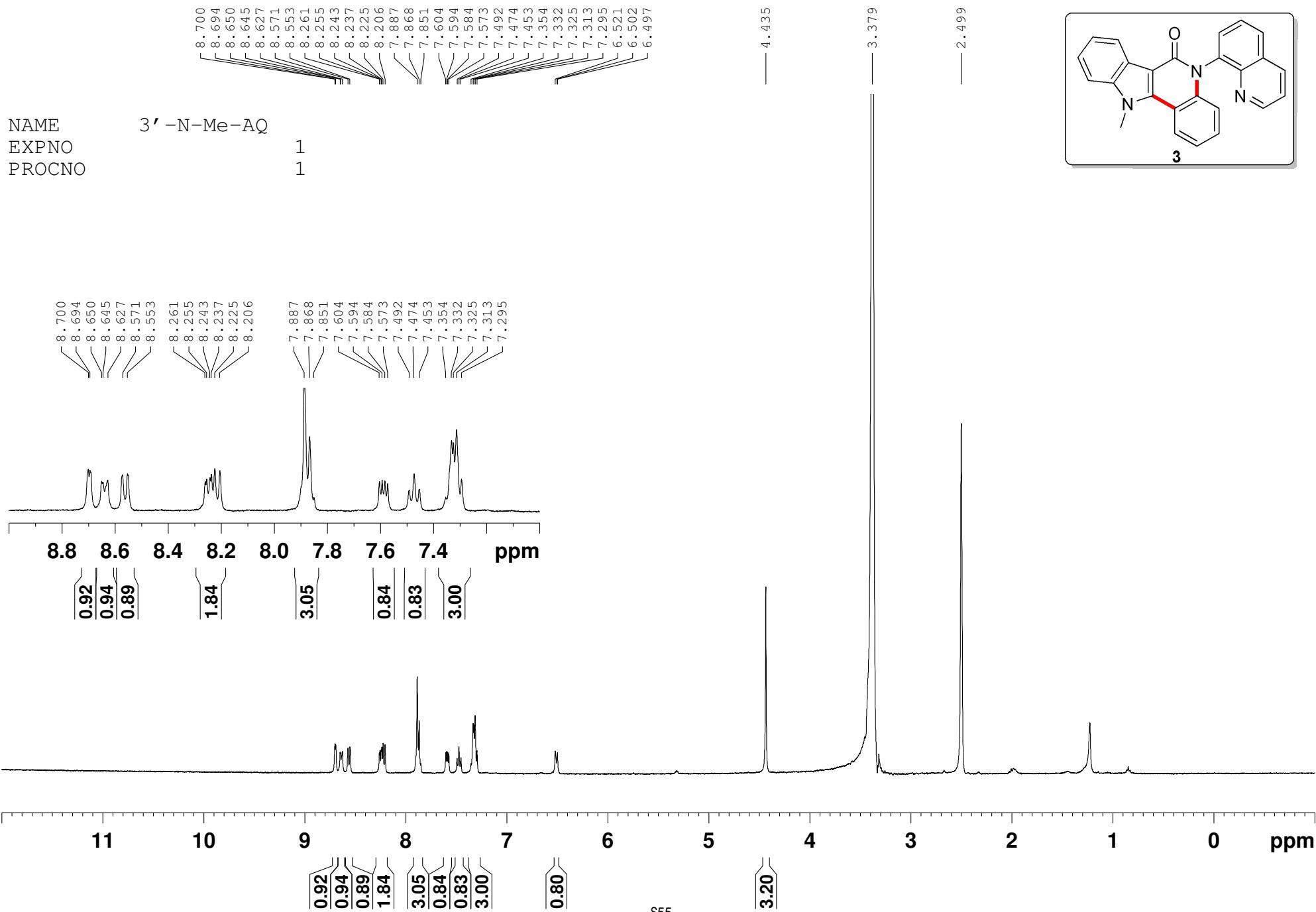




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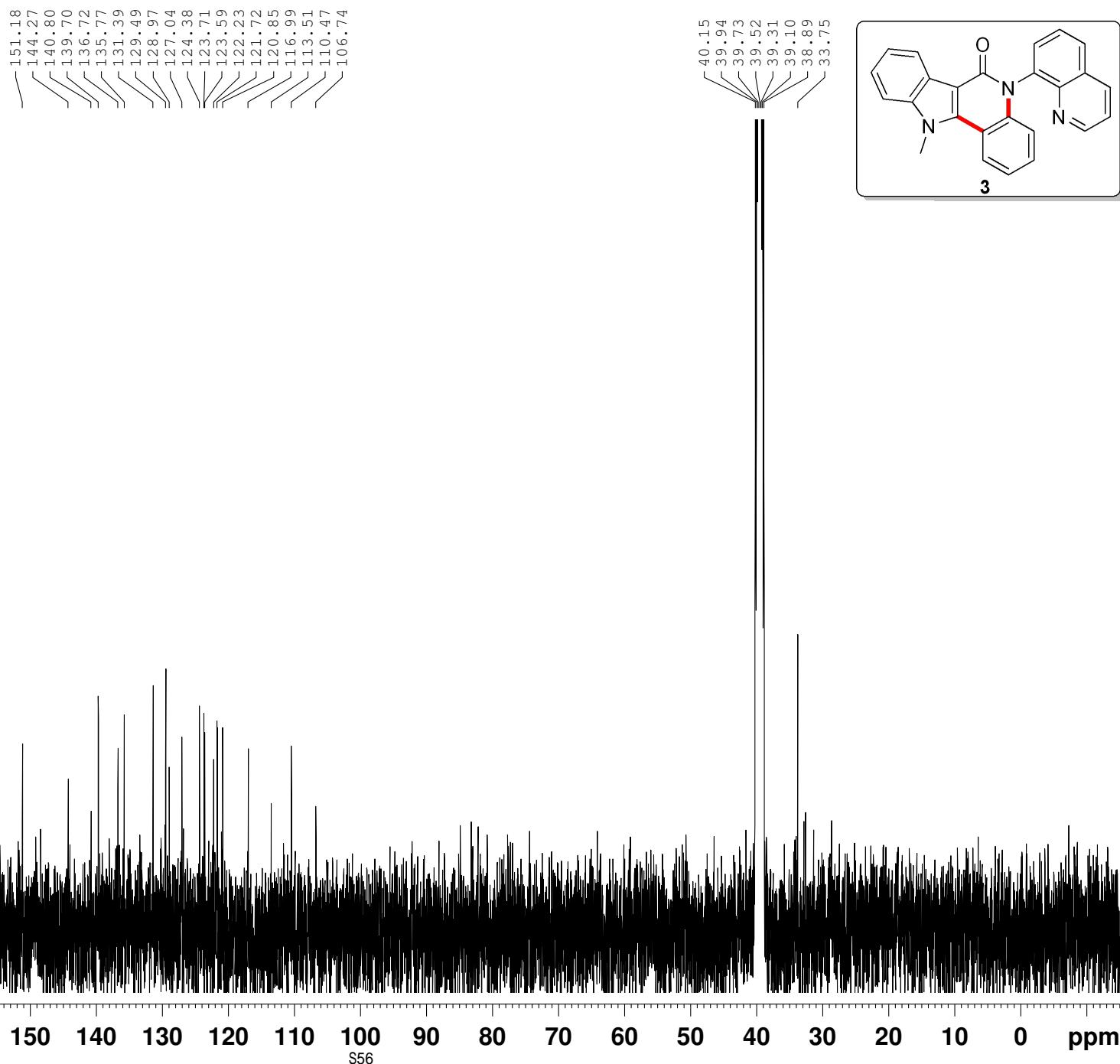
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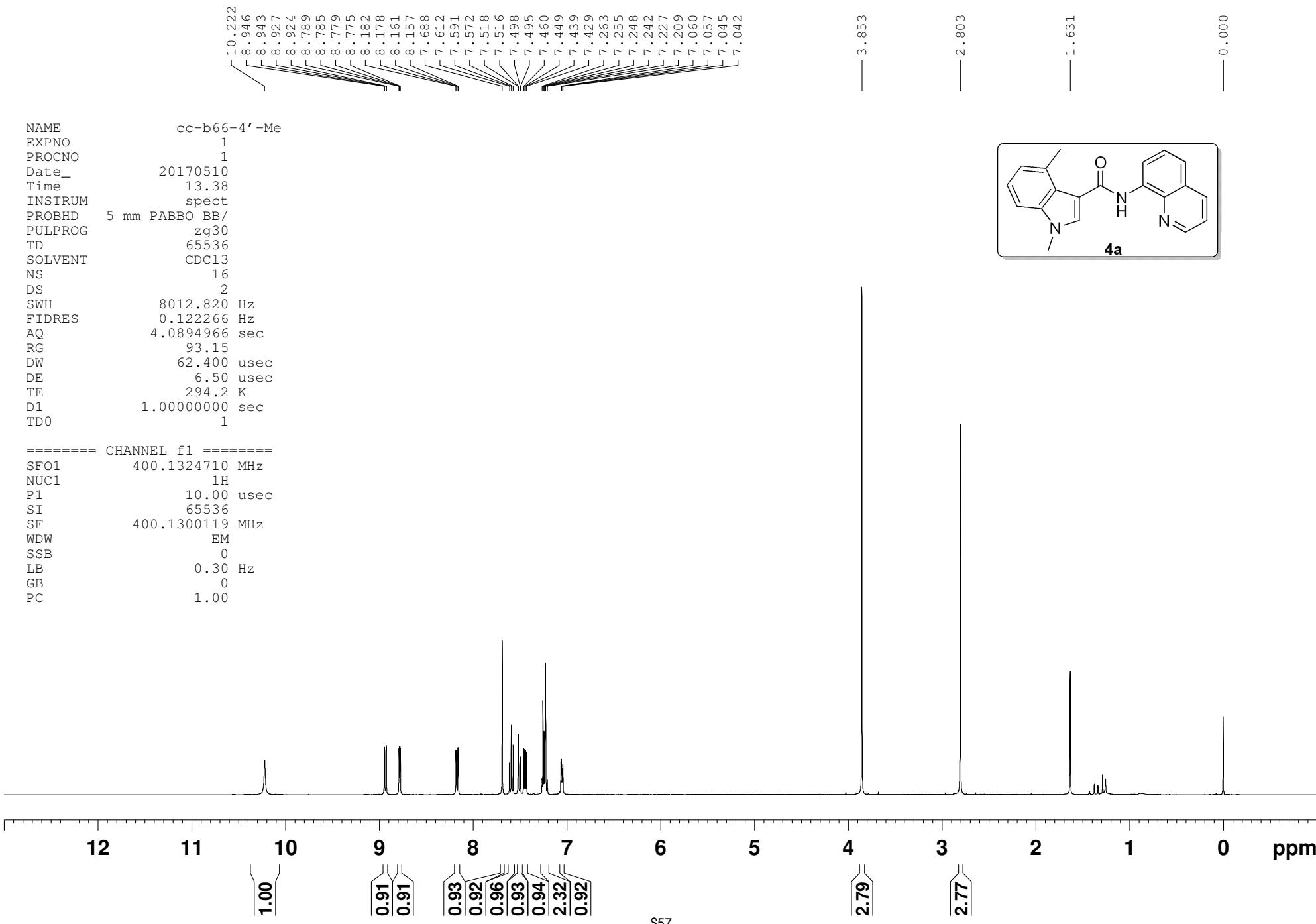


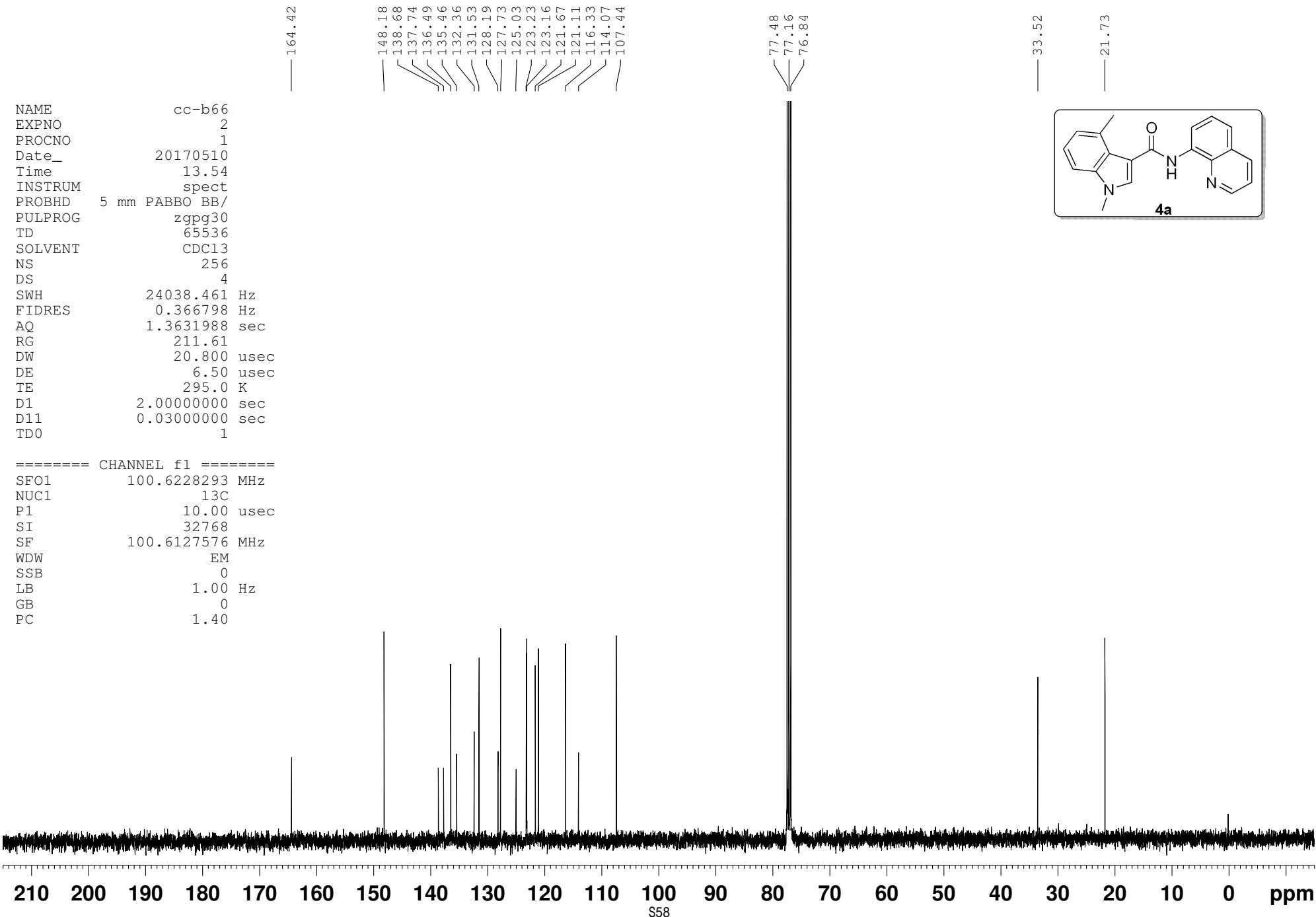


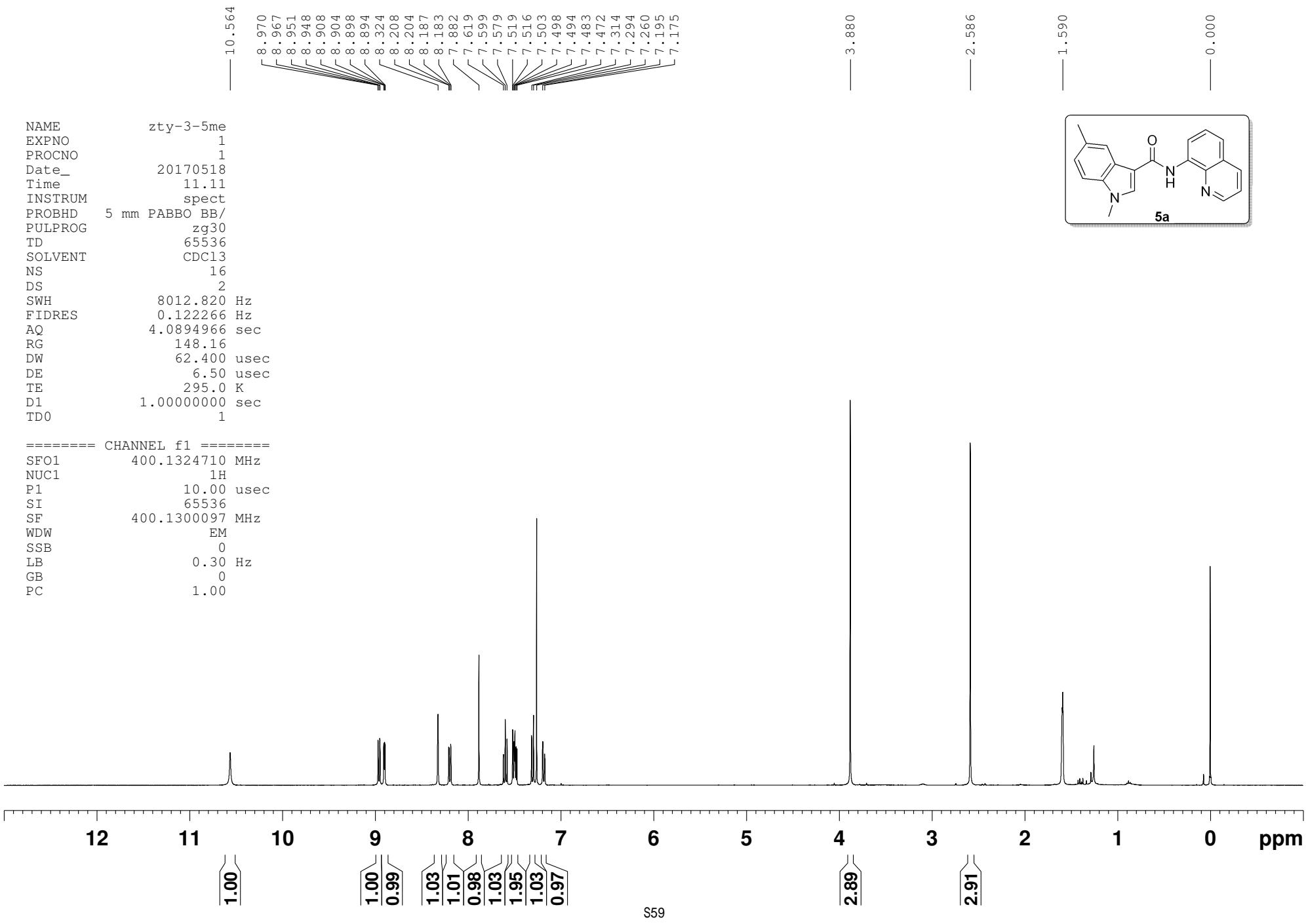
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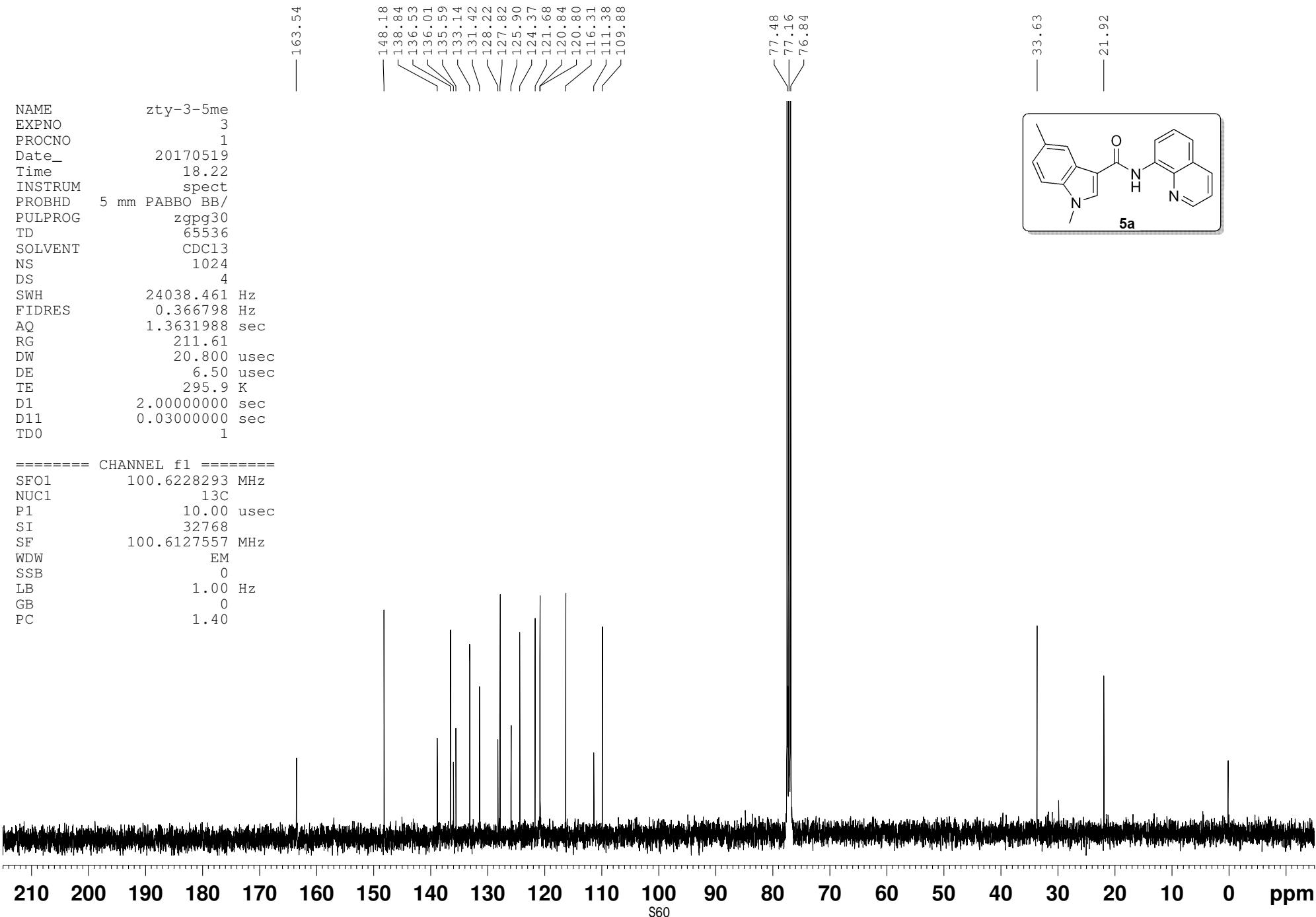
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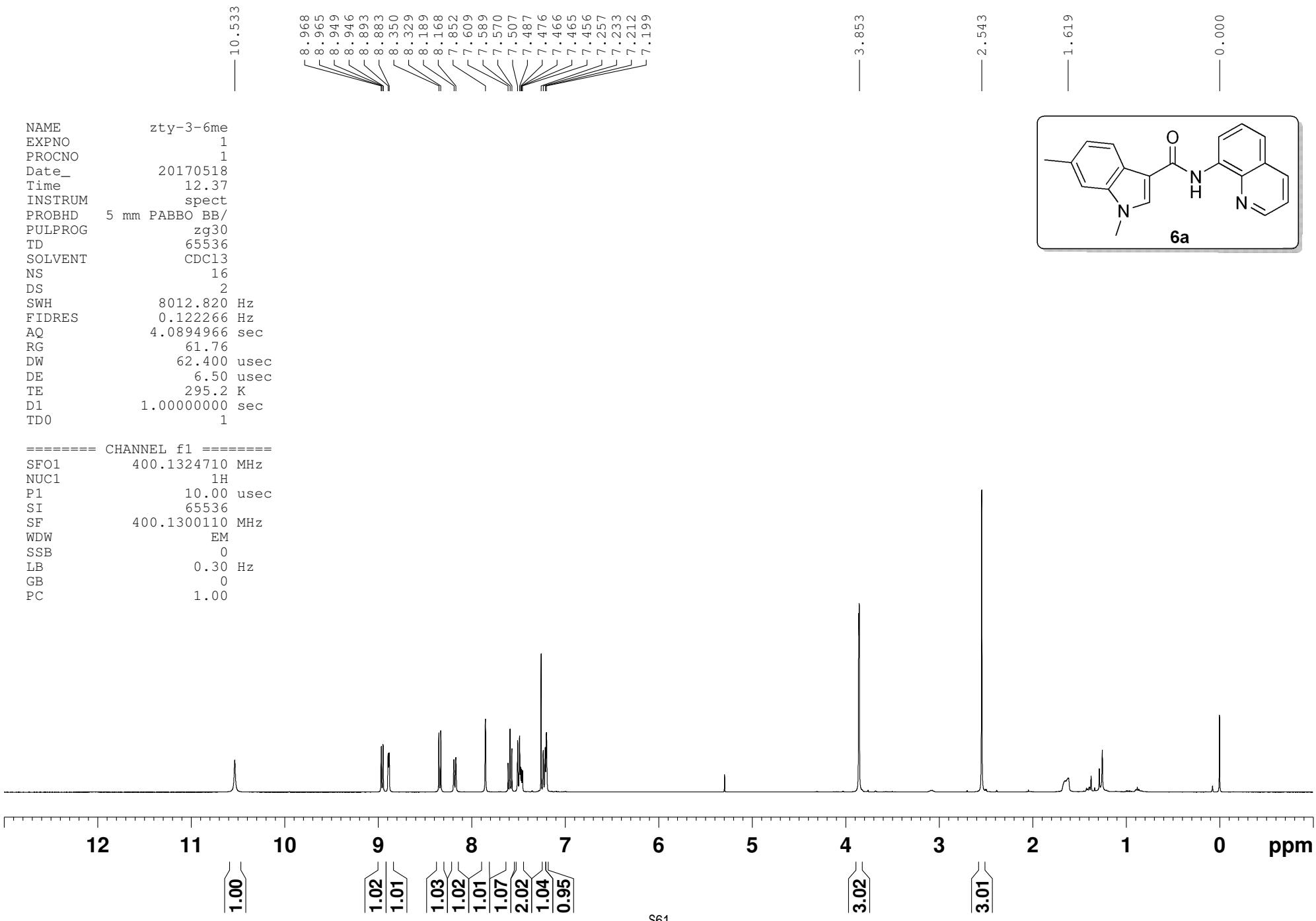


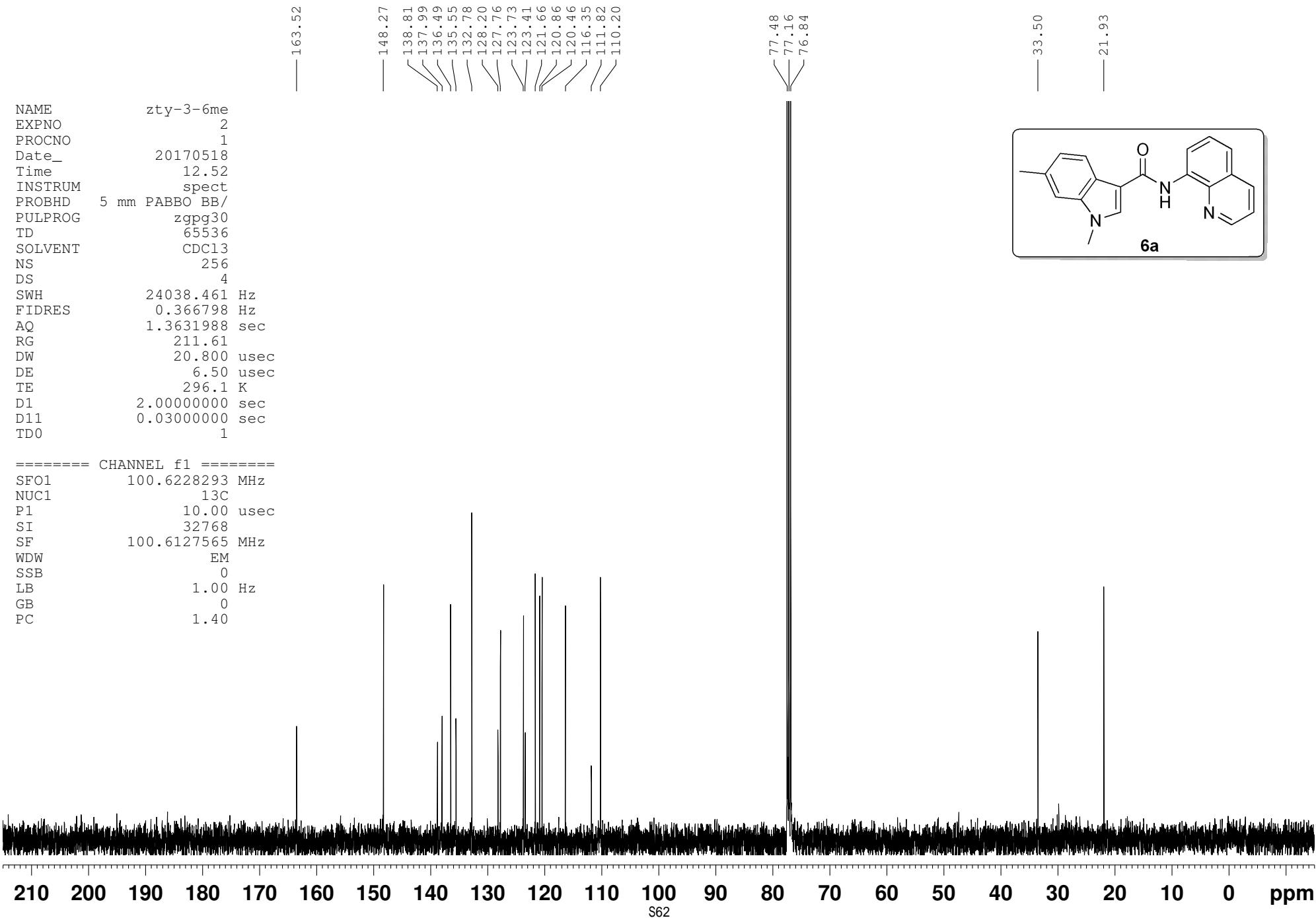


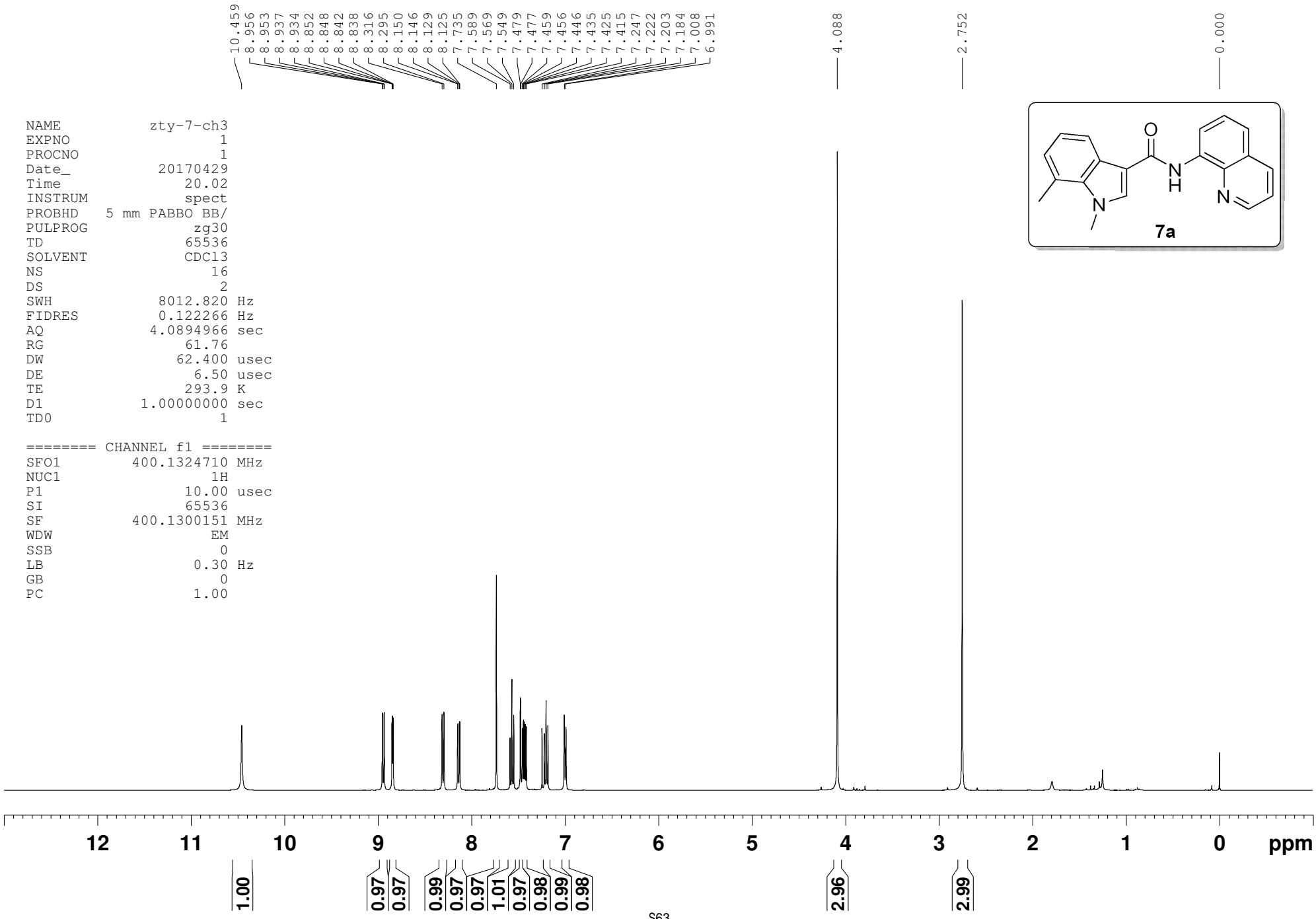


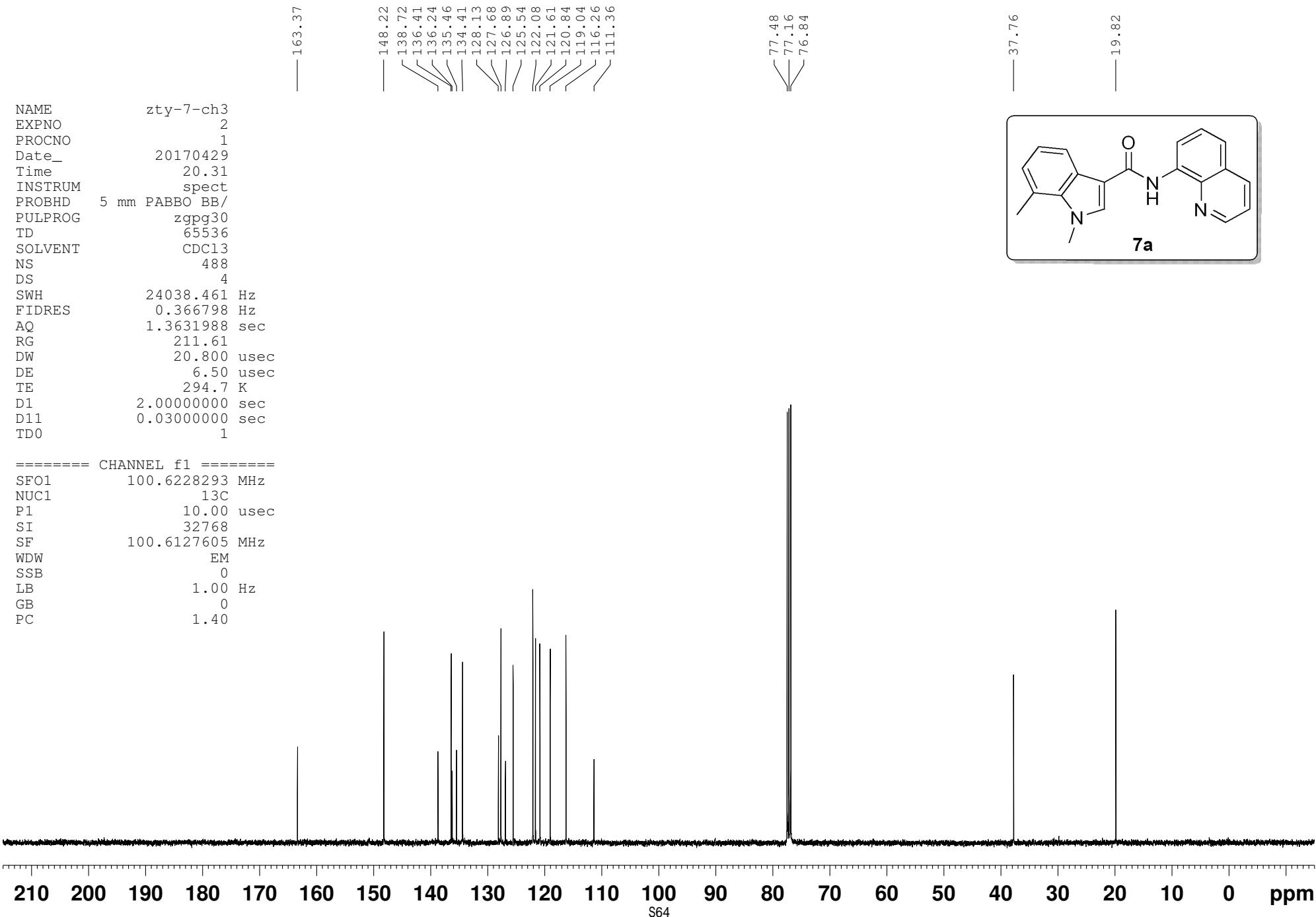


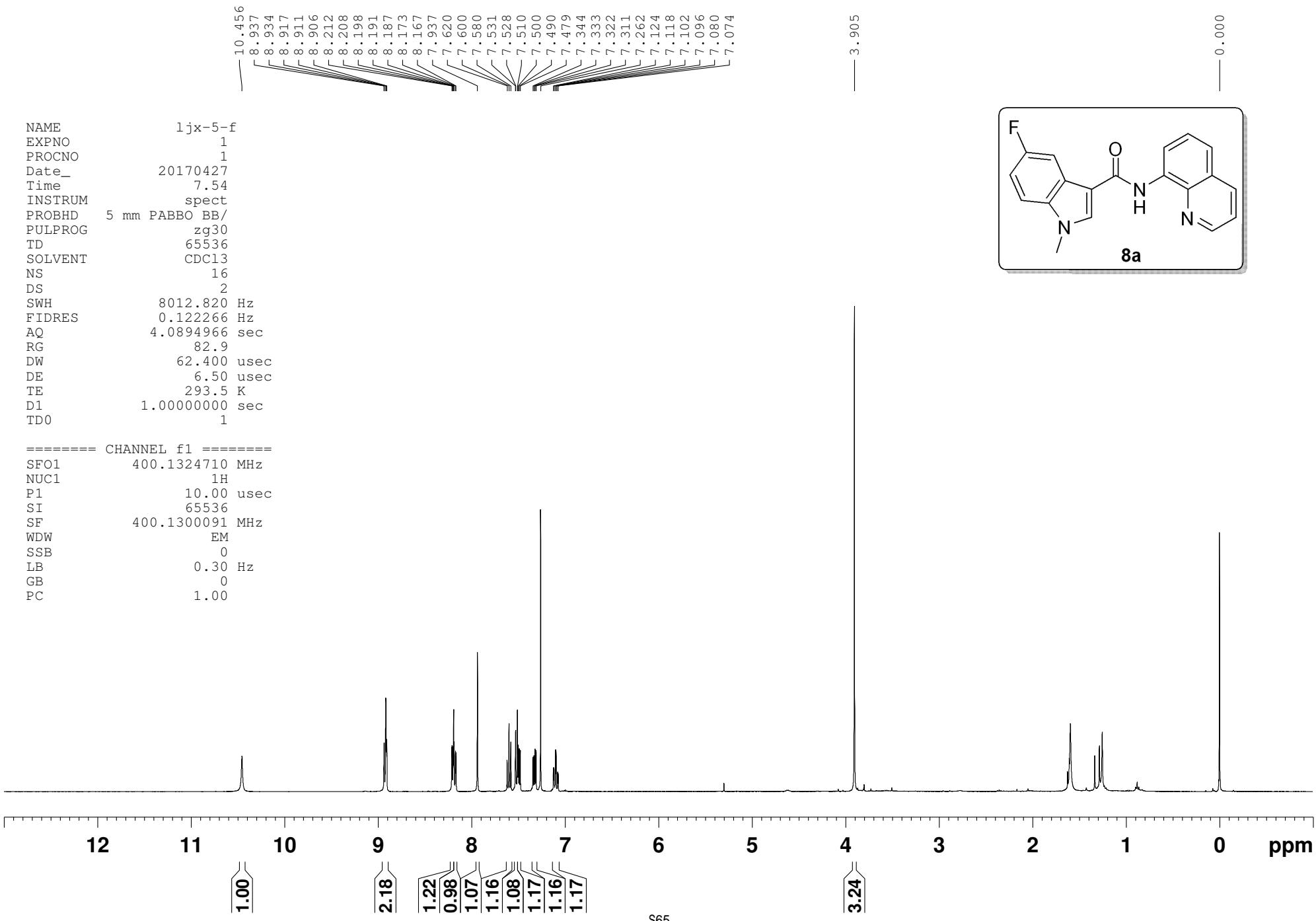


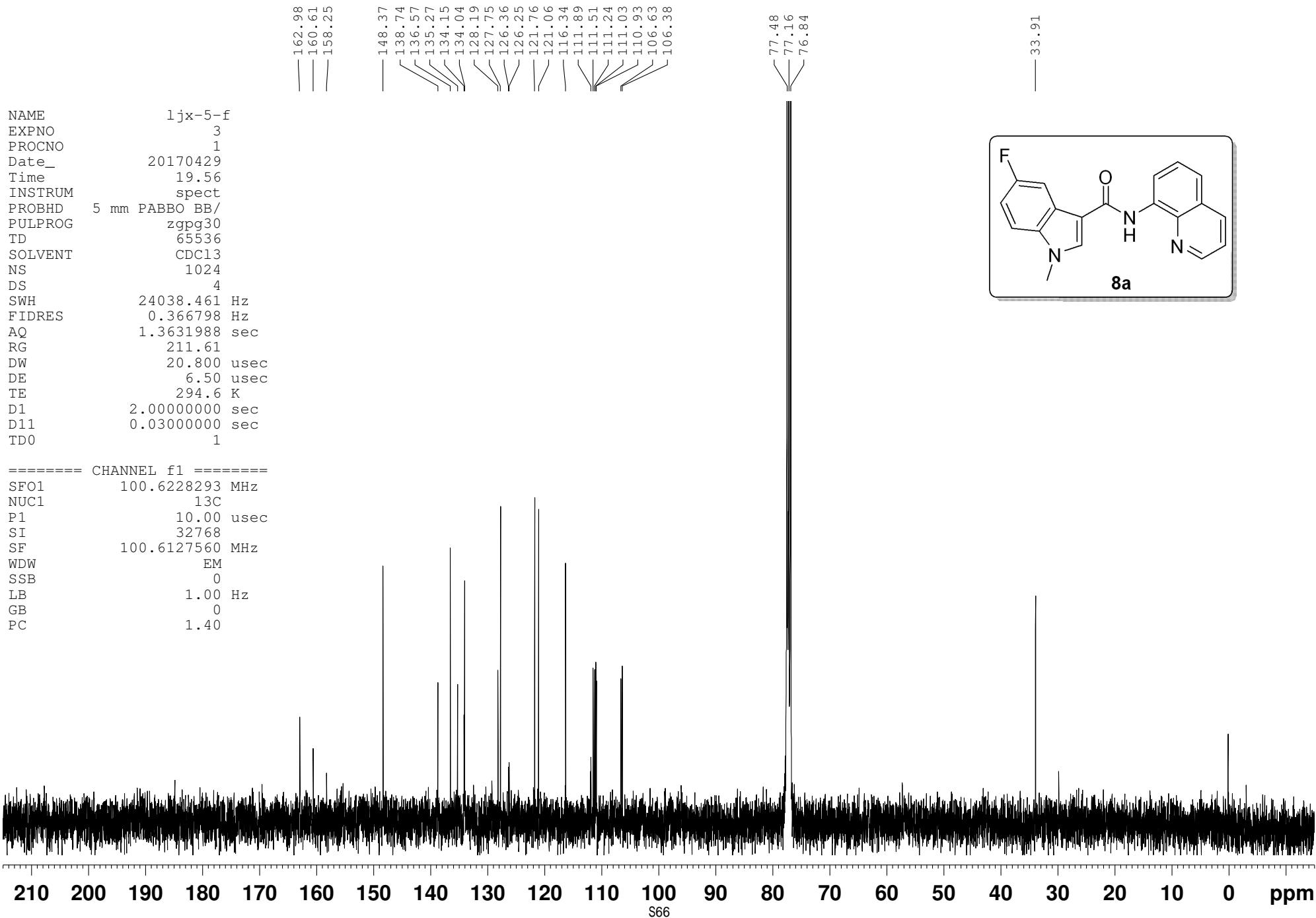


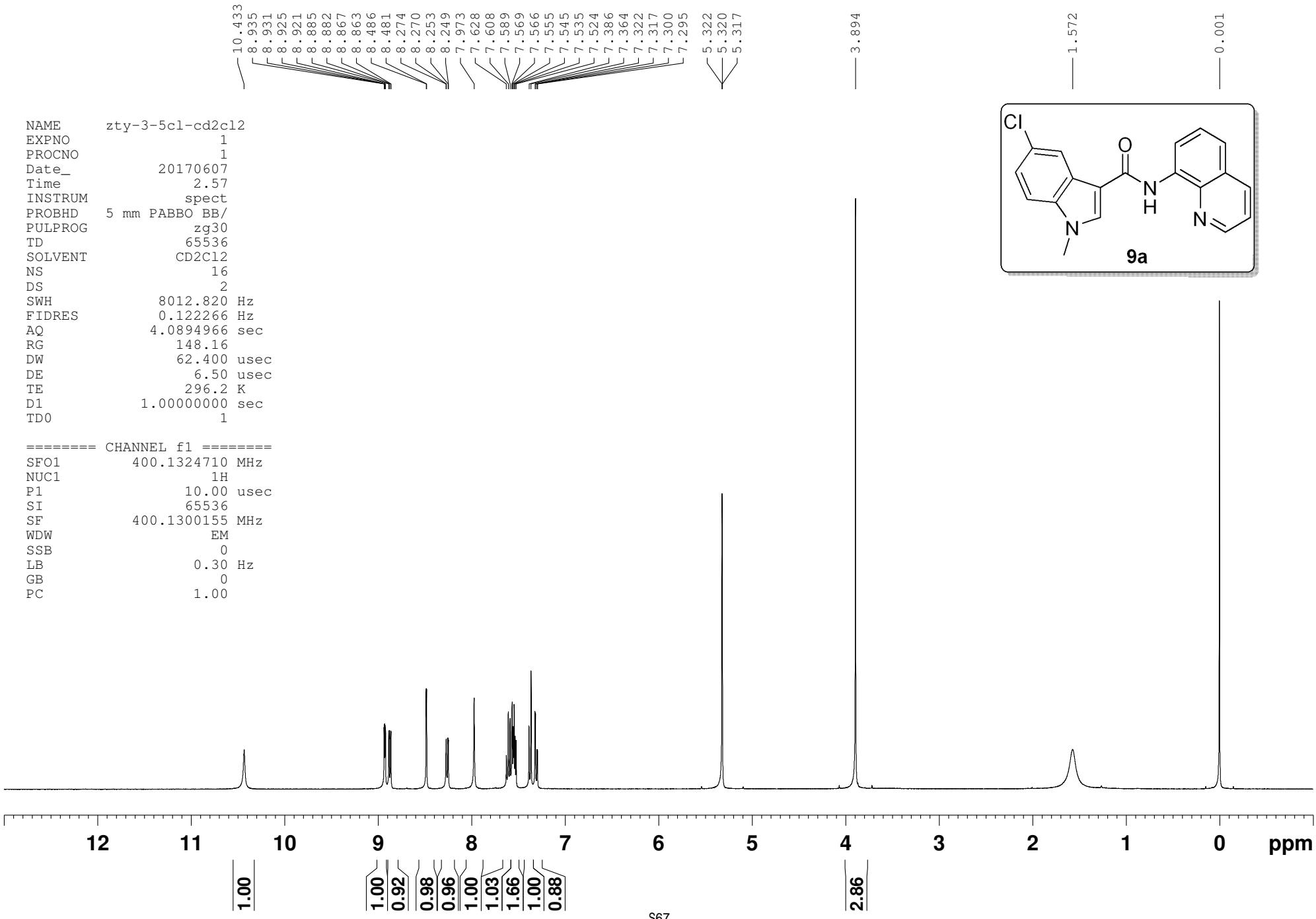


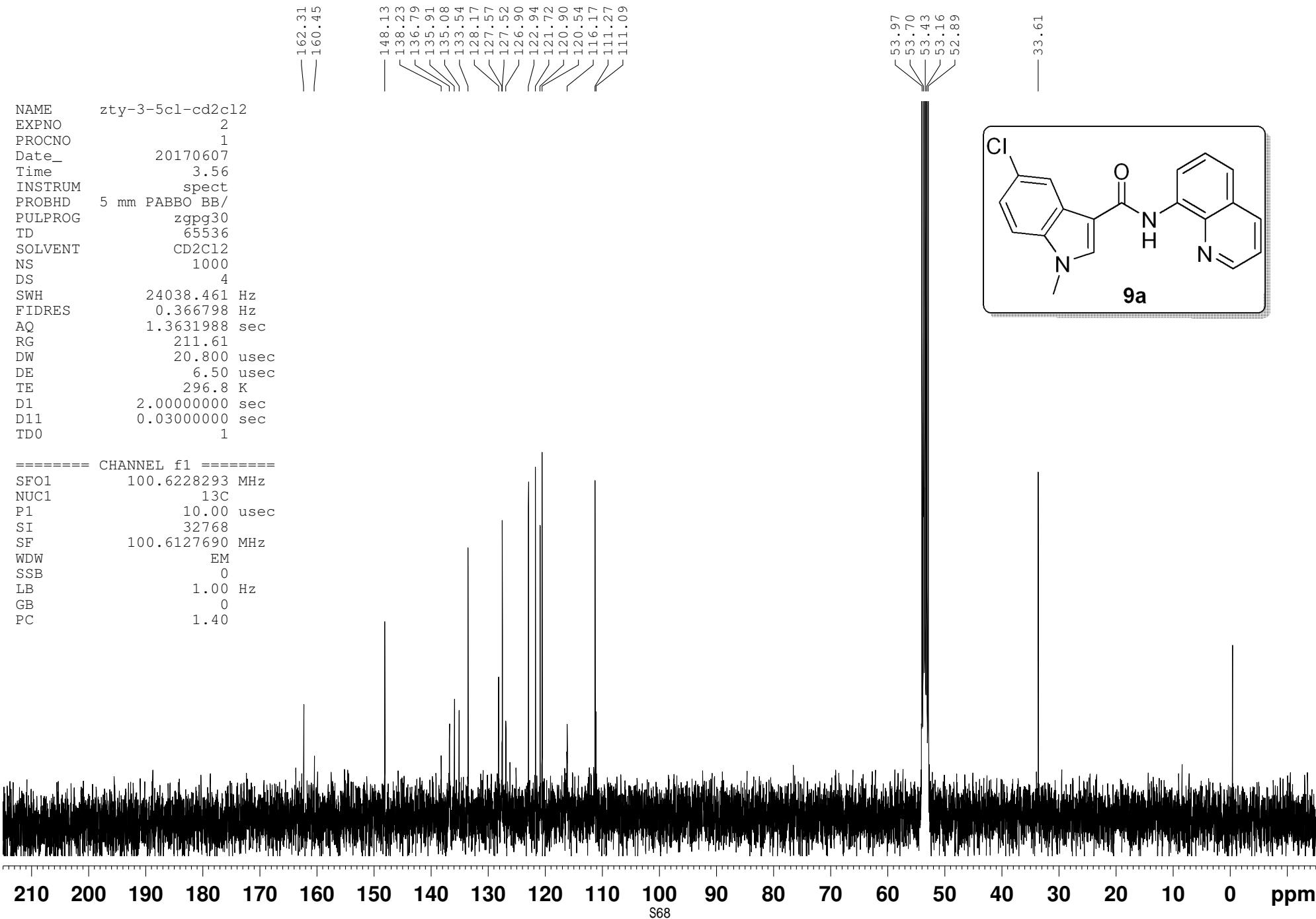


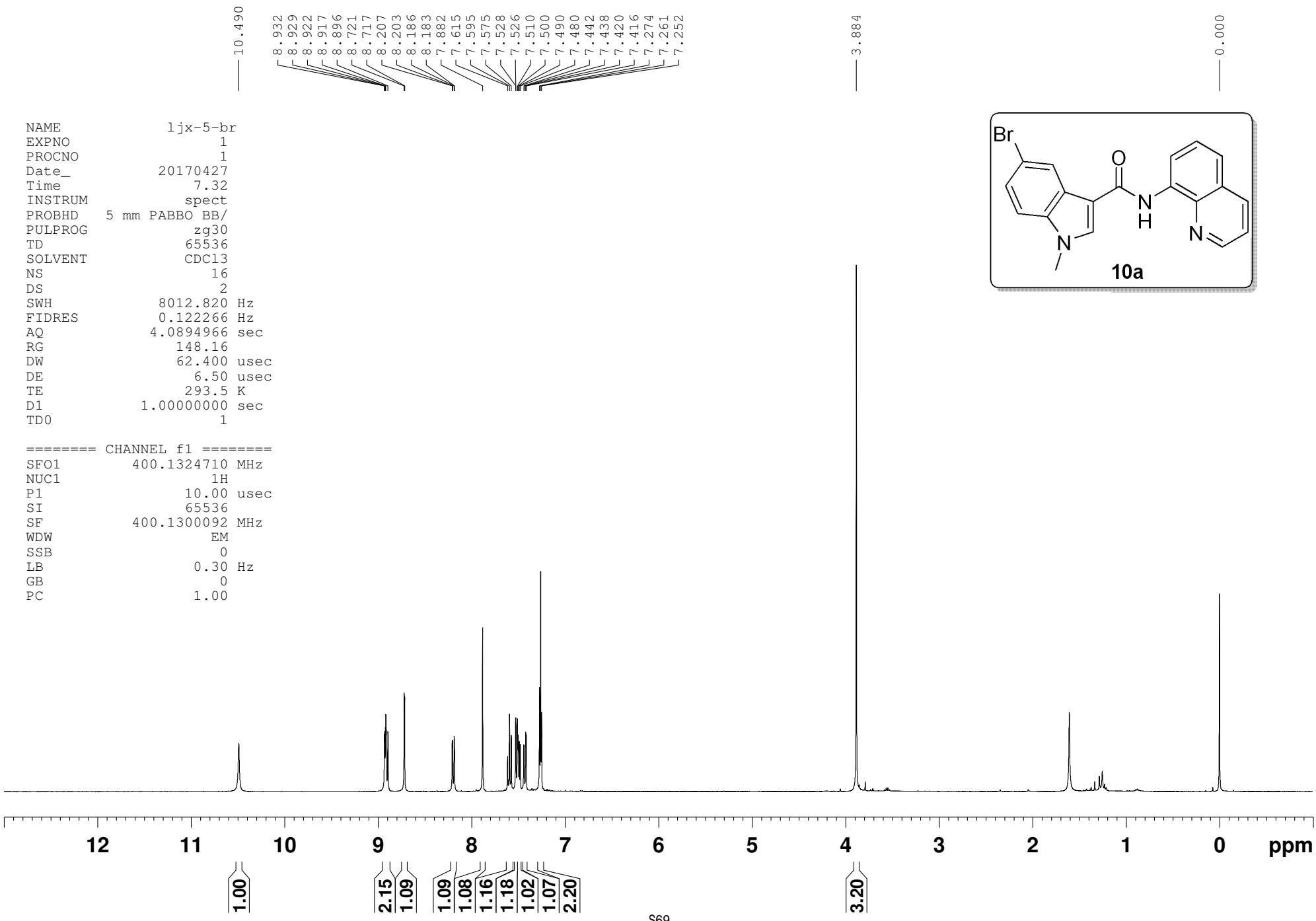


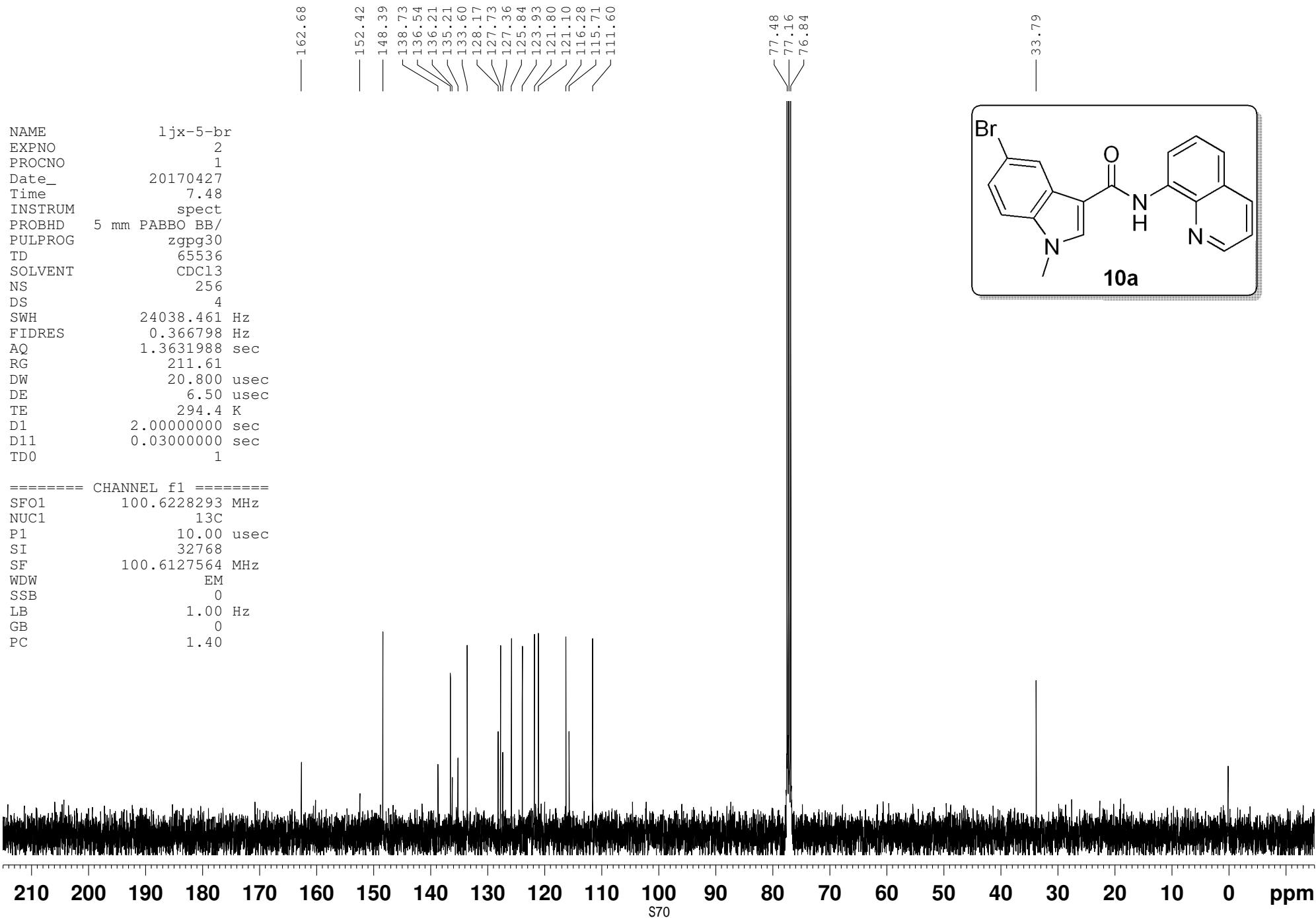


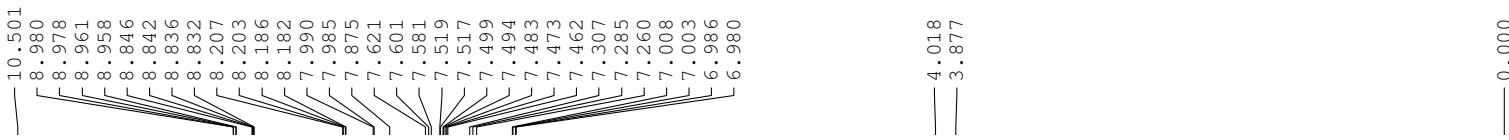






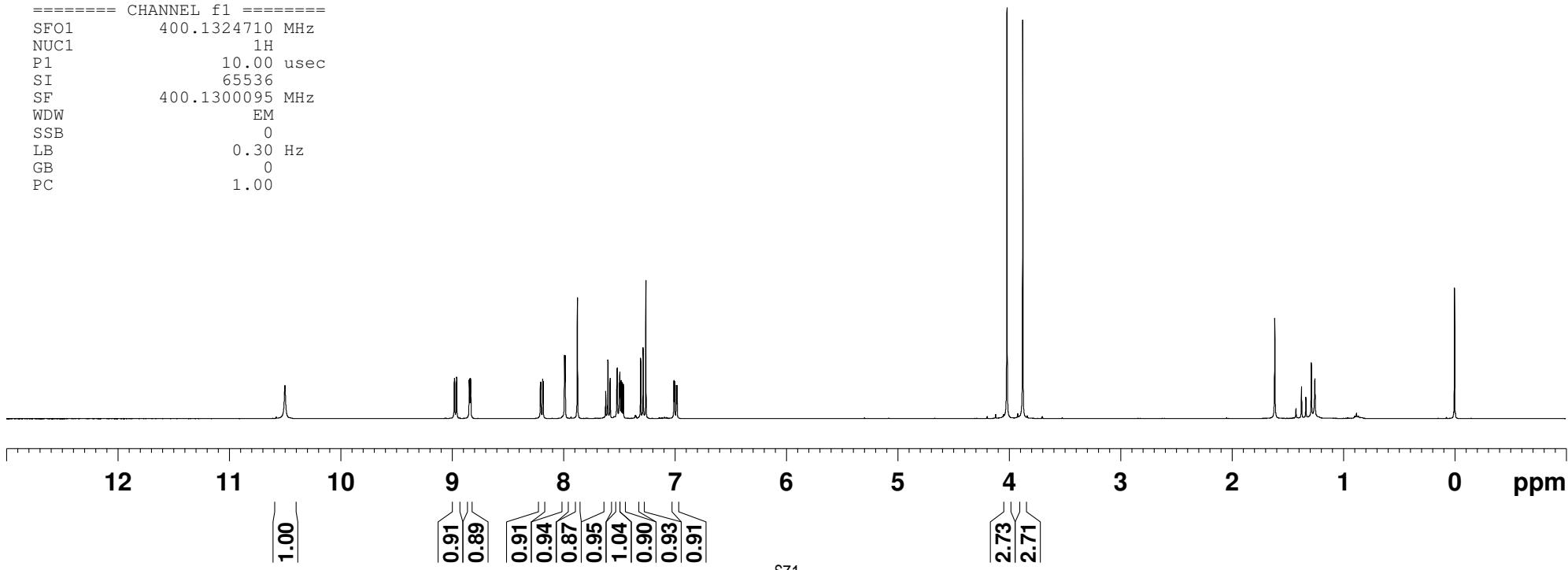






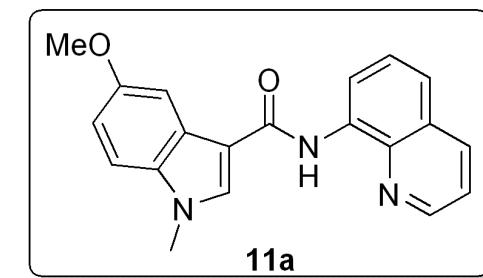
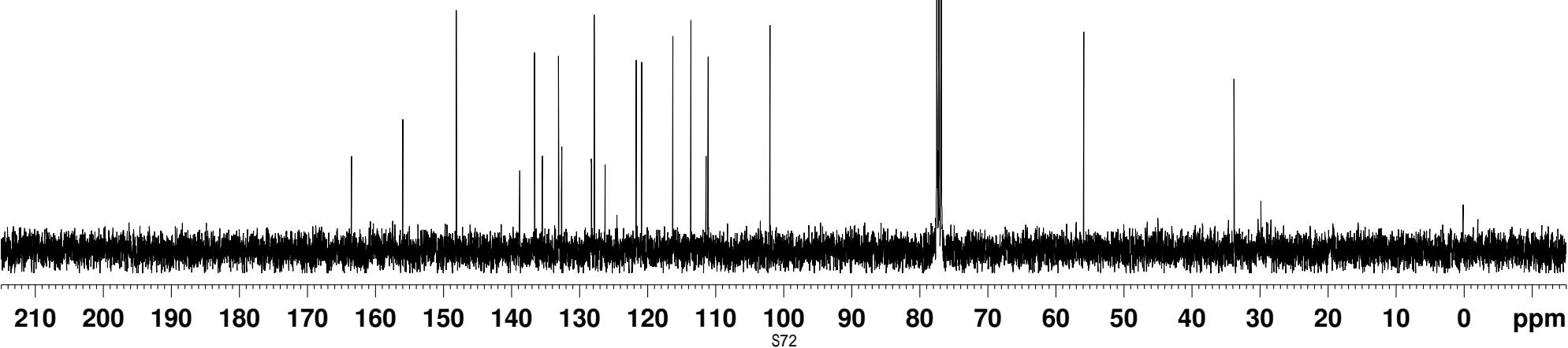
NAME 1.jx-5-meo
 EXPNO 1
 PROCNO 1
 Date_ 20170427
 Time 12.08
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zg30
 TD 65536
 SOLVENT CDCl₃
 NS 16
 DS 2
 SWH 8012.820 Hz
 FIDRES 0.122266 Hz
 AQ 4.0894966 sec
 RG 131.08
 DW 62.400 usec
 DE 6.50 usec
 TE 293.7 K
 D1 1.00000000 sec
 TDO 1

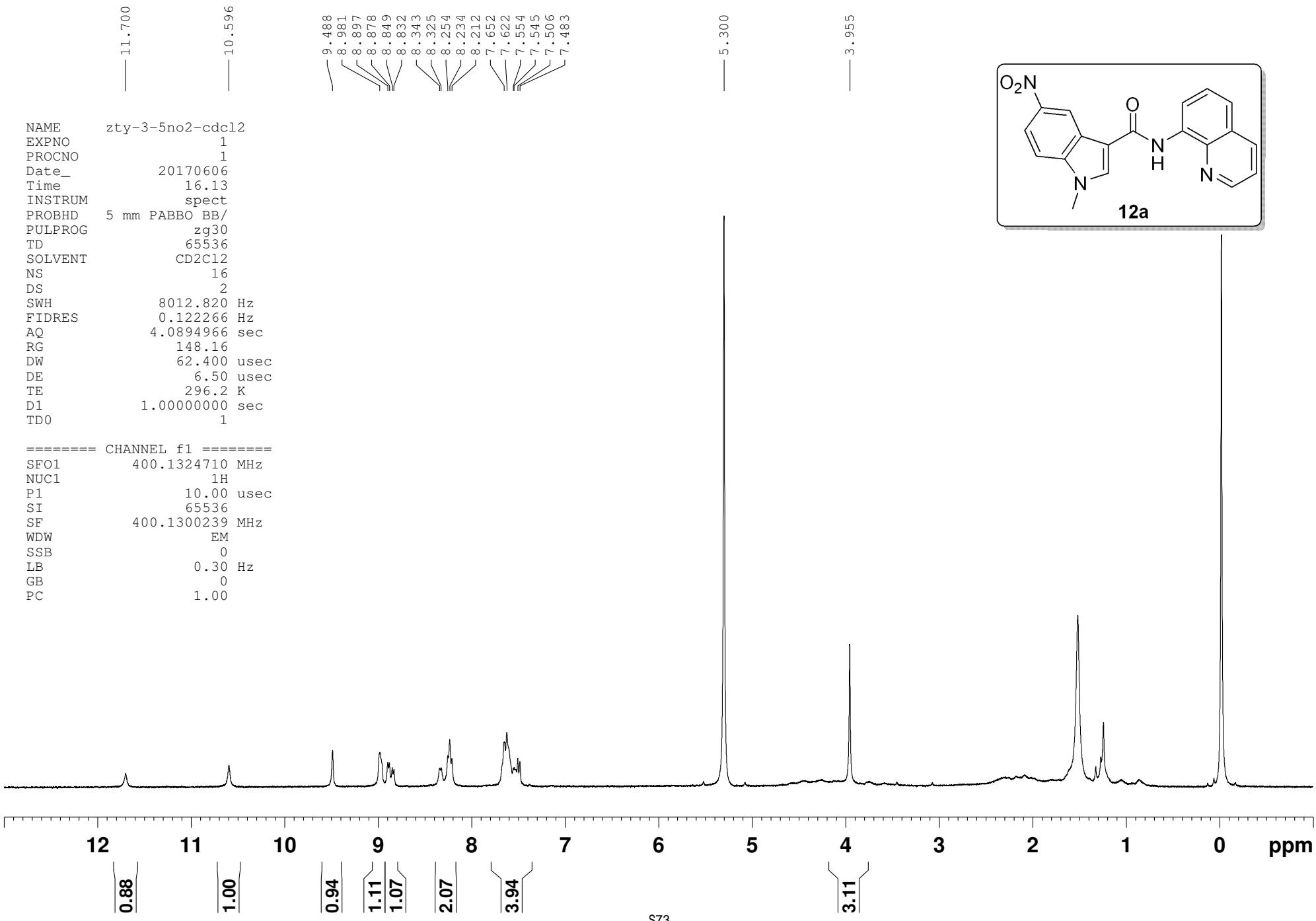
===== CHANNEL f1 =====
 SFO1 400.1324710 MHz
 NUC1 1H
 P1 10.00 usec
 SI 65536
 SF 400.1300095 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

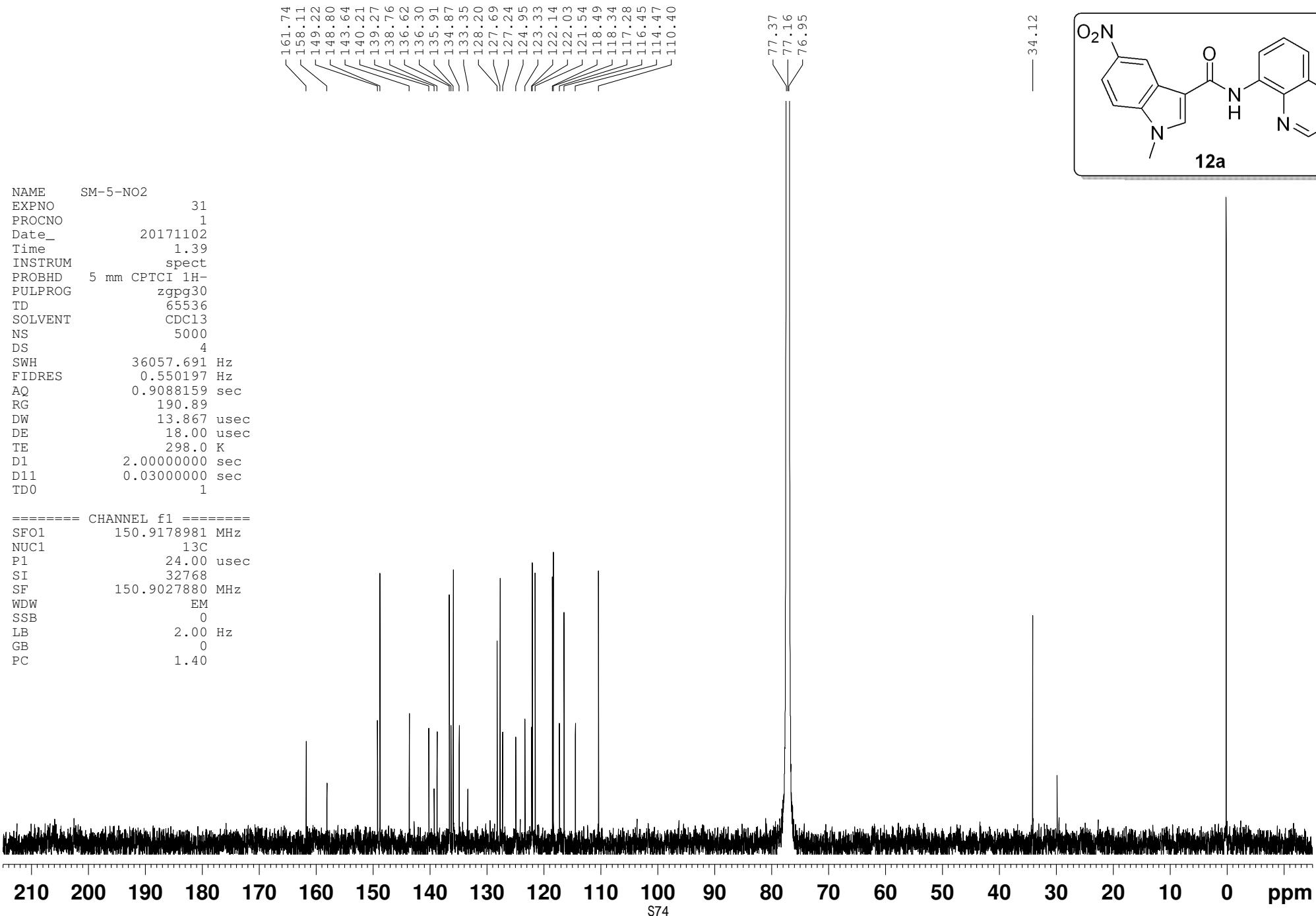


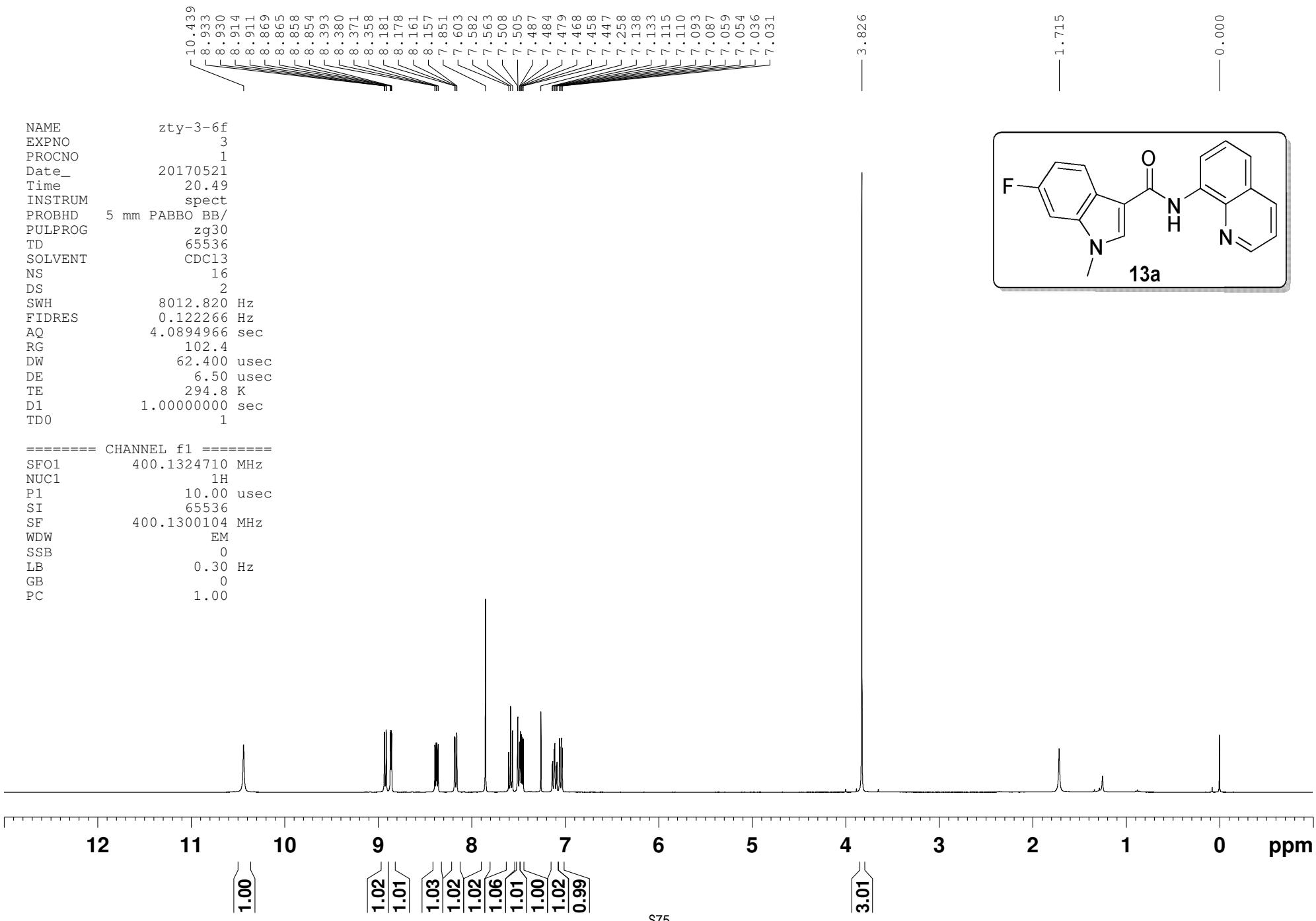
NAME 1.jx-5-meo
 EXPNO 2
 PROCNO 1
 Date_ 20170427
 Time 12.24
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 256
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631988 sec
 RG 211.61
 DW 20.800 usec
 DE 6.50 usec
 TE 294.5 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

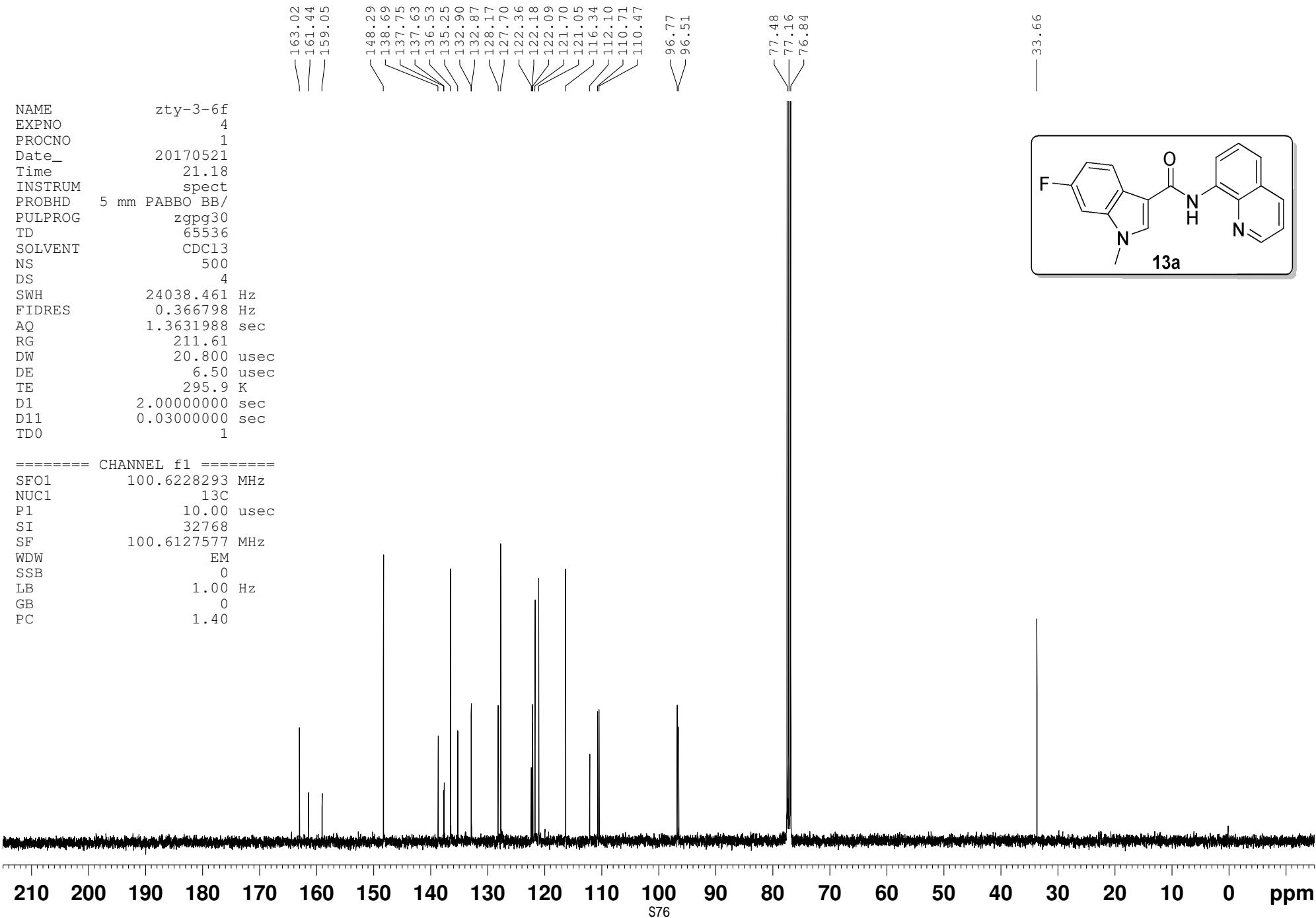
===== CHANNEL f1 =====
 SFO1 100.6228293 MHz
 NUC1 13C
 P1 10.00 usec
 SI 32768
 SF 100.6127564 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

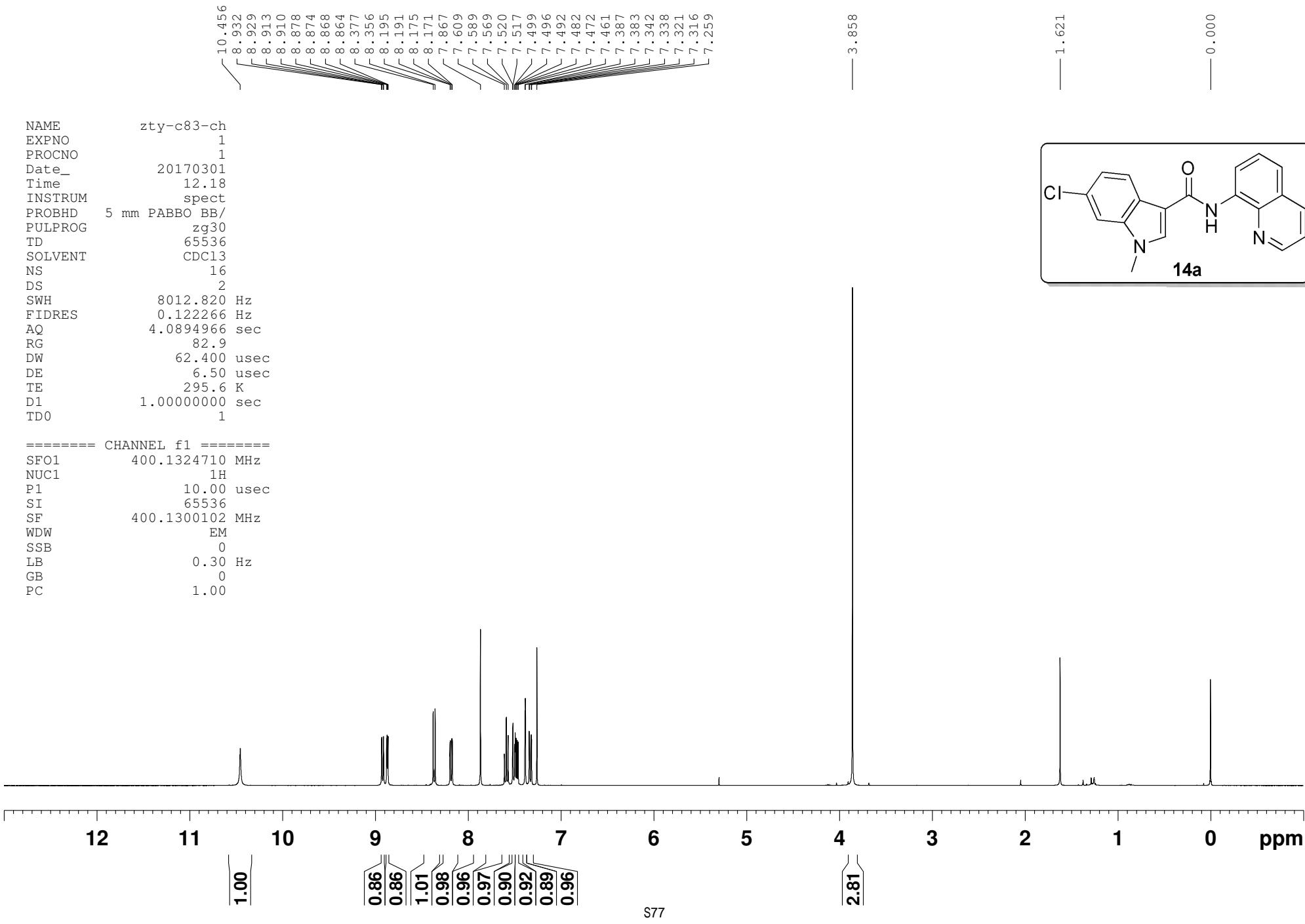






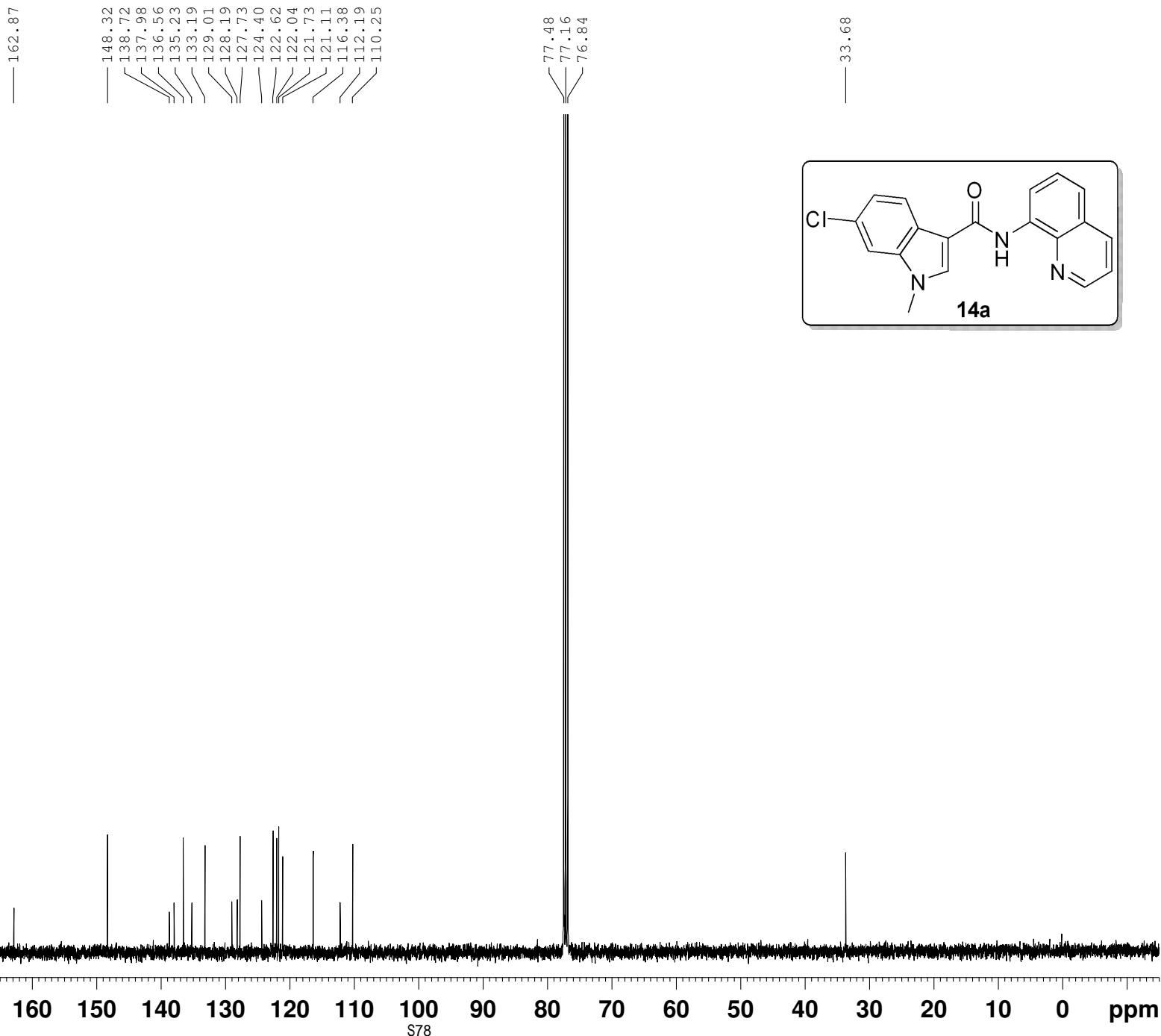


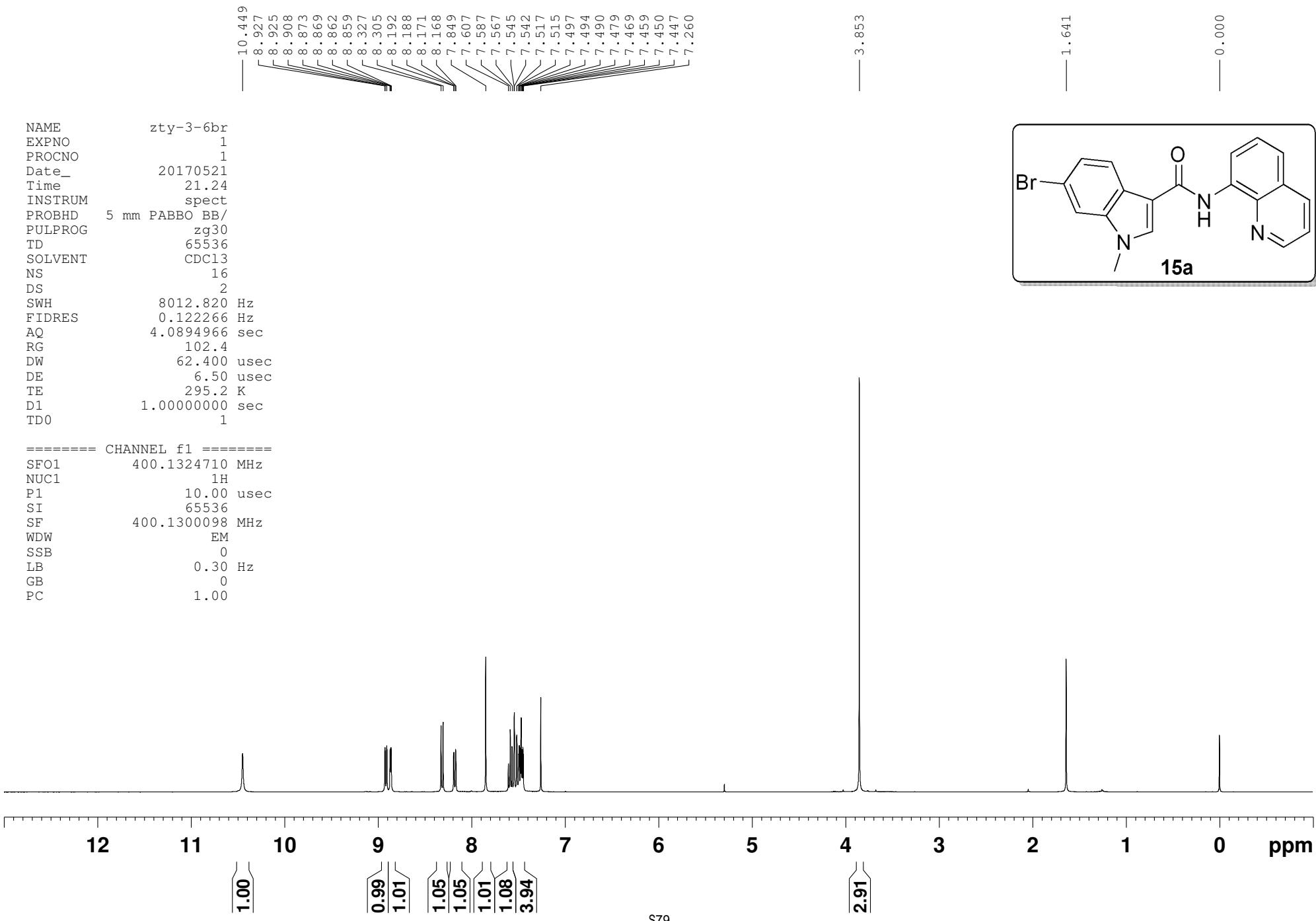


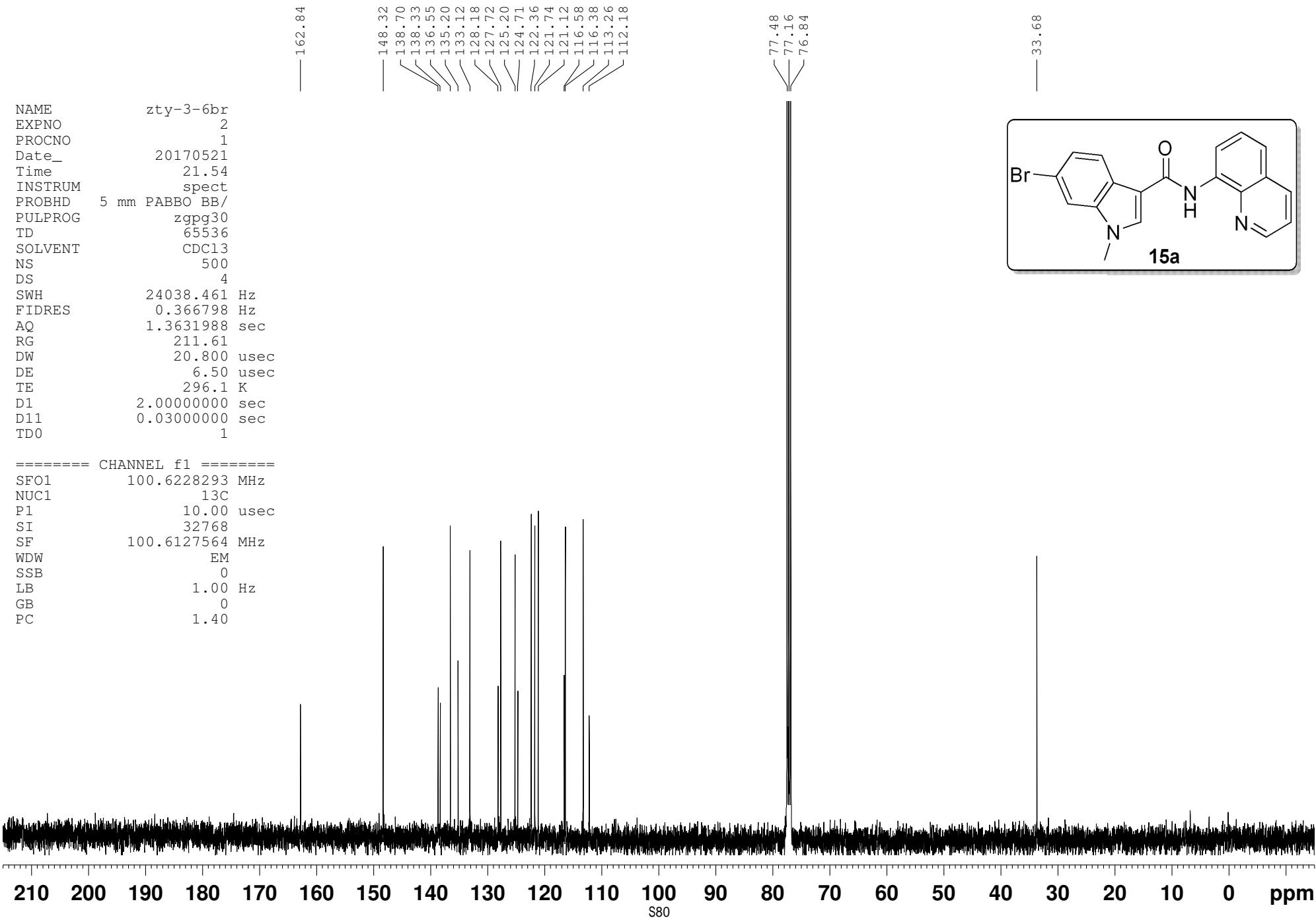


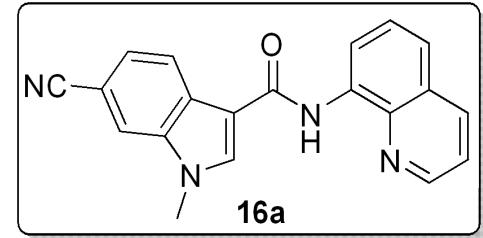
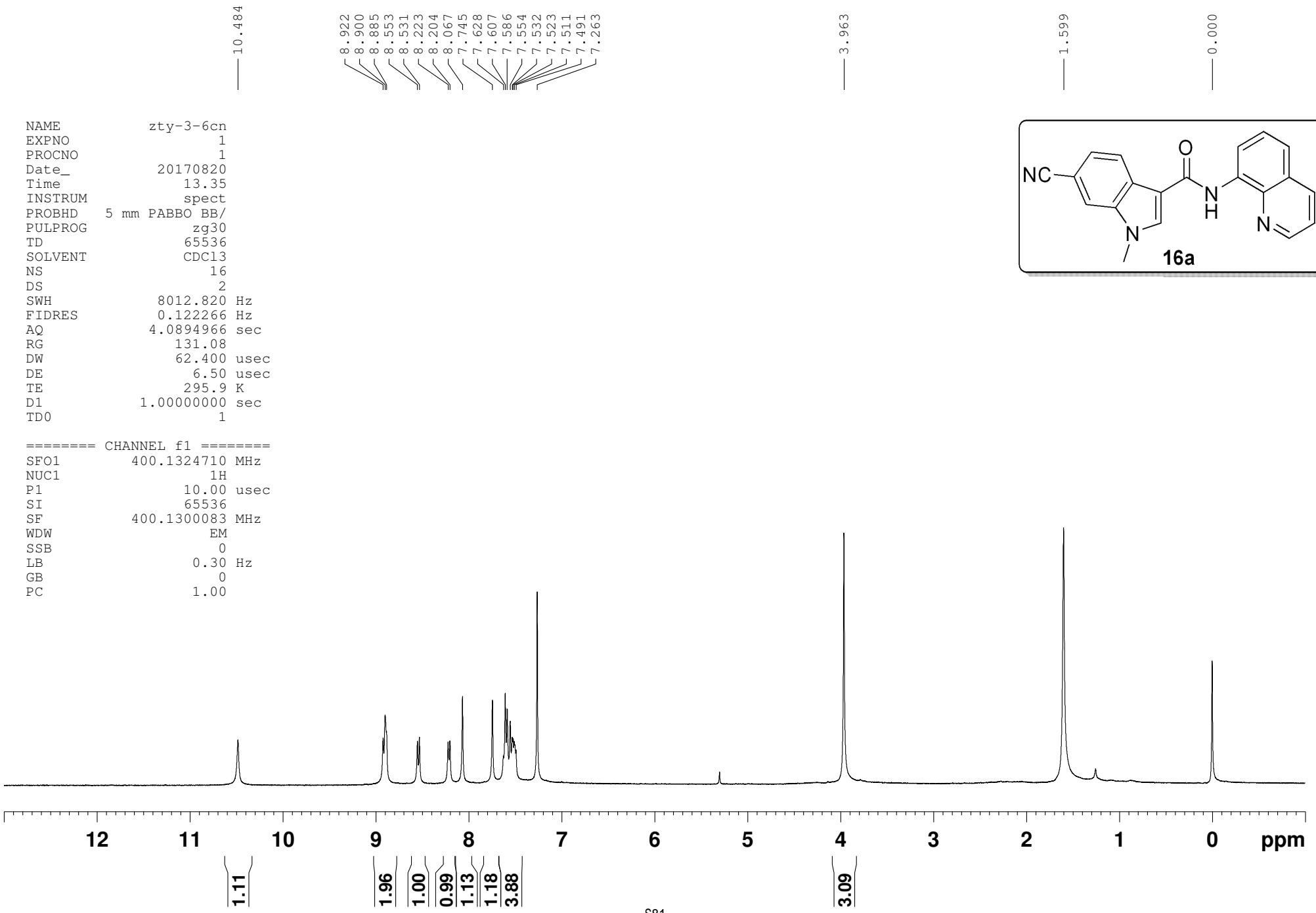
NAME zty-c83-ch
 EXPNO 2
 PROCNO 1
 Date_ 20170301
 Time 12.34
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 256
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631988 sec
 RG 211.61
 DW 20.800 usec
 DE 6.50 usec
 TE 296.4 K
 D1 2.0000000 sec
 D11 0.03000000 sec
 TDO 1

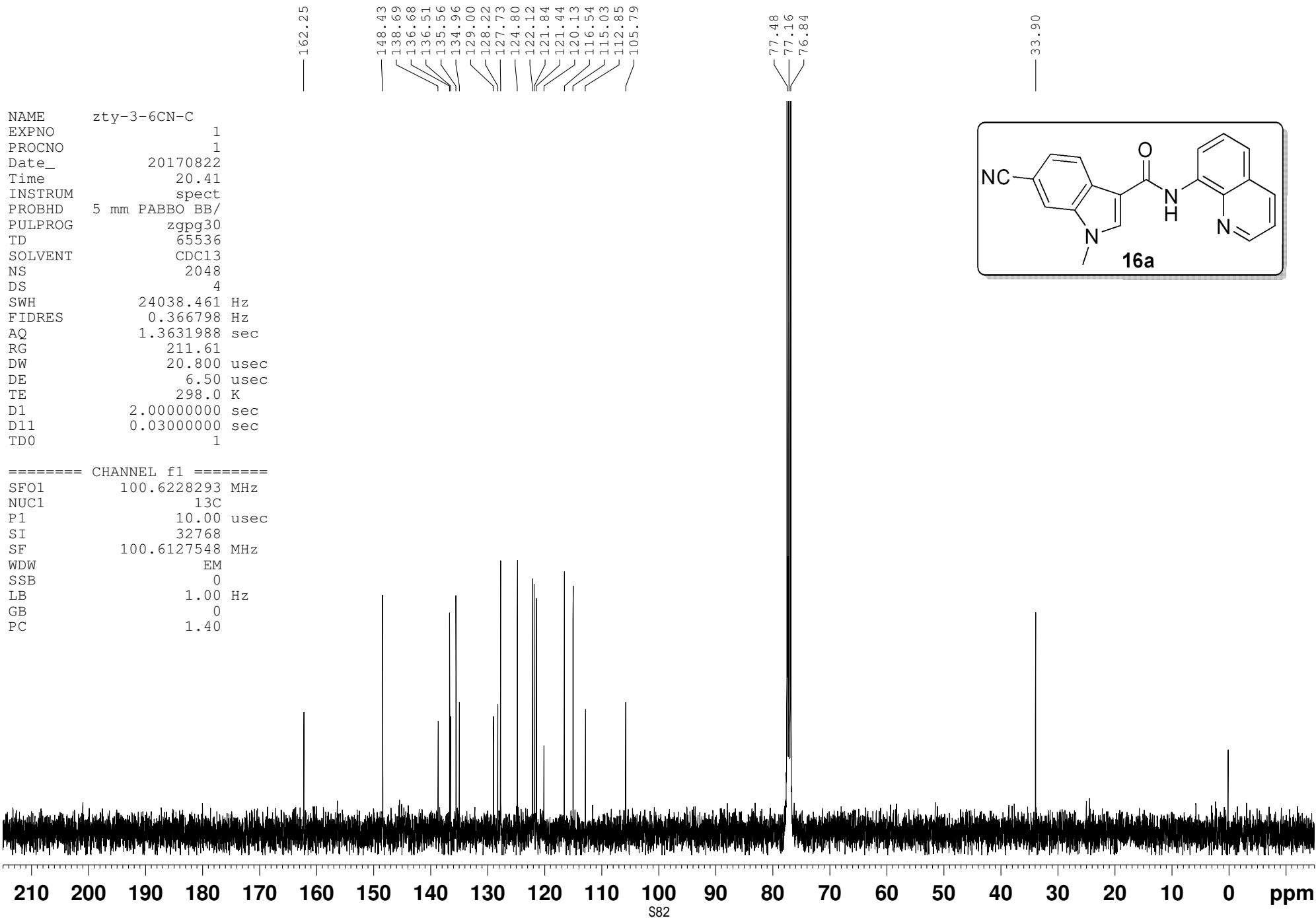
===== CHANNEL f1 =====
 SFO1 100.6228293 MHz
 NUC1 13C
 P1 10.00 usec
 SI 32768
 SF 100.6127562 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

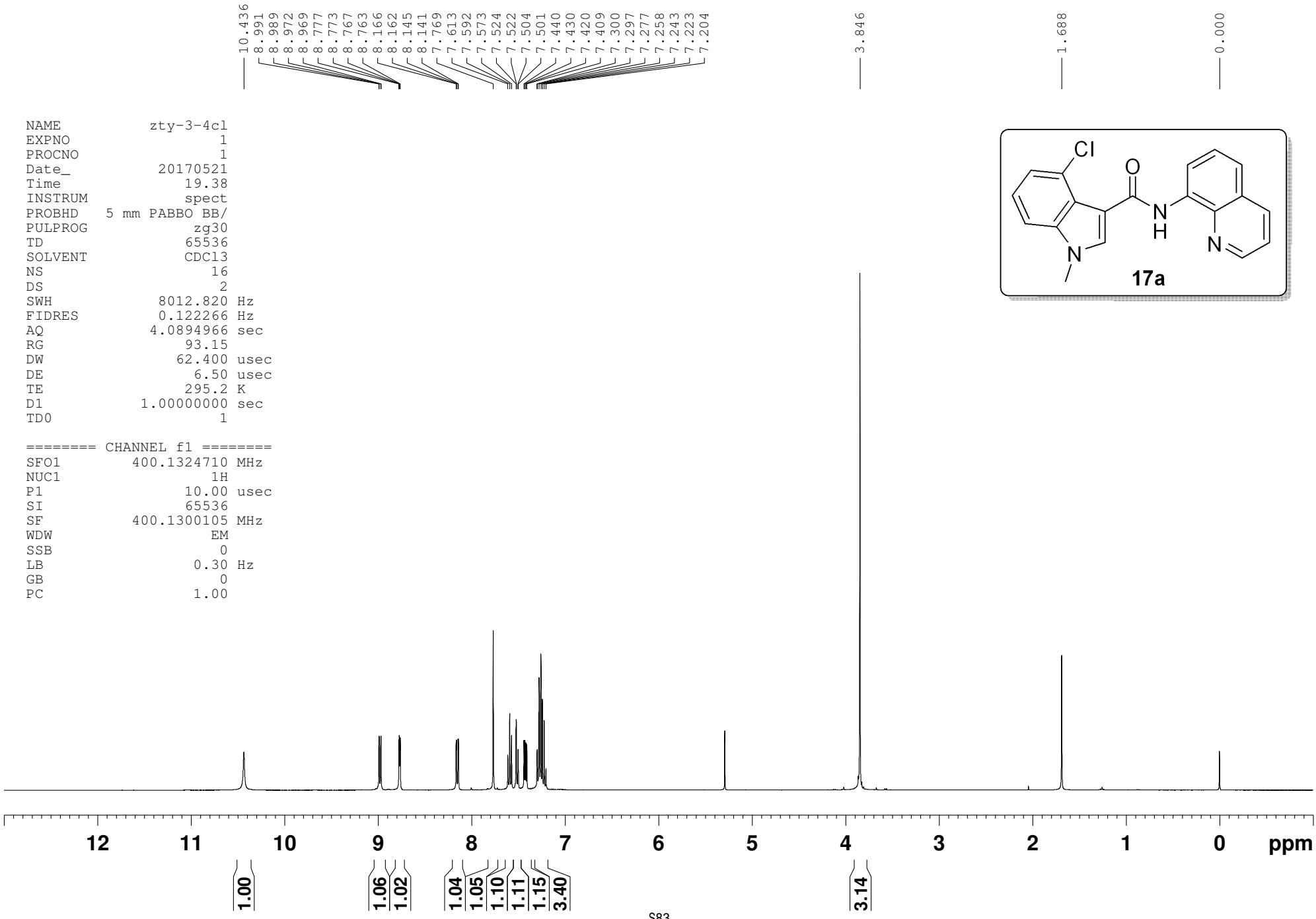


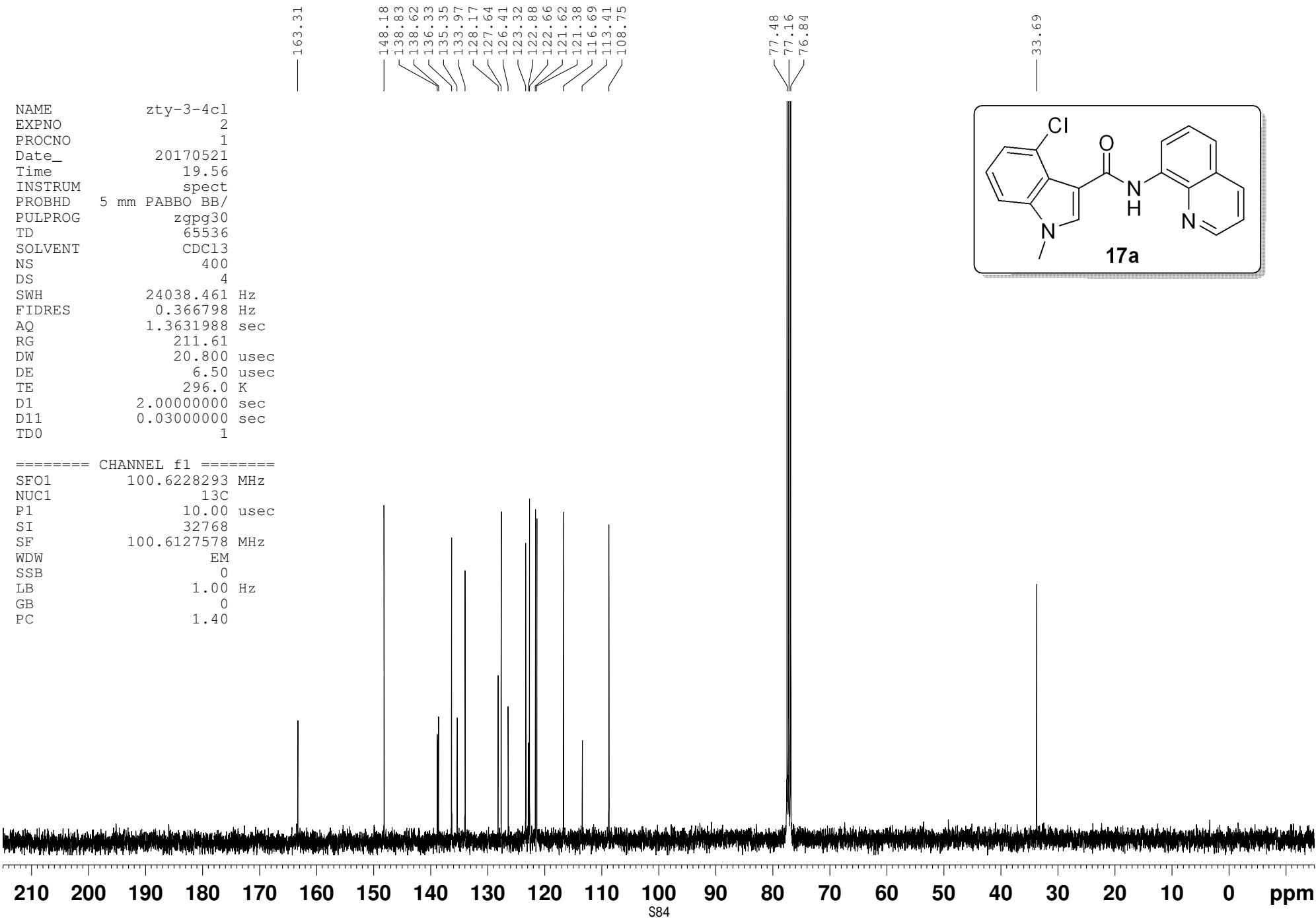


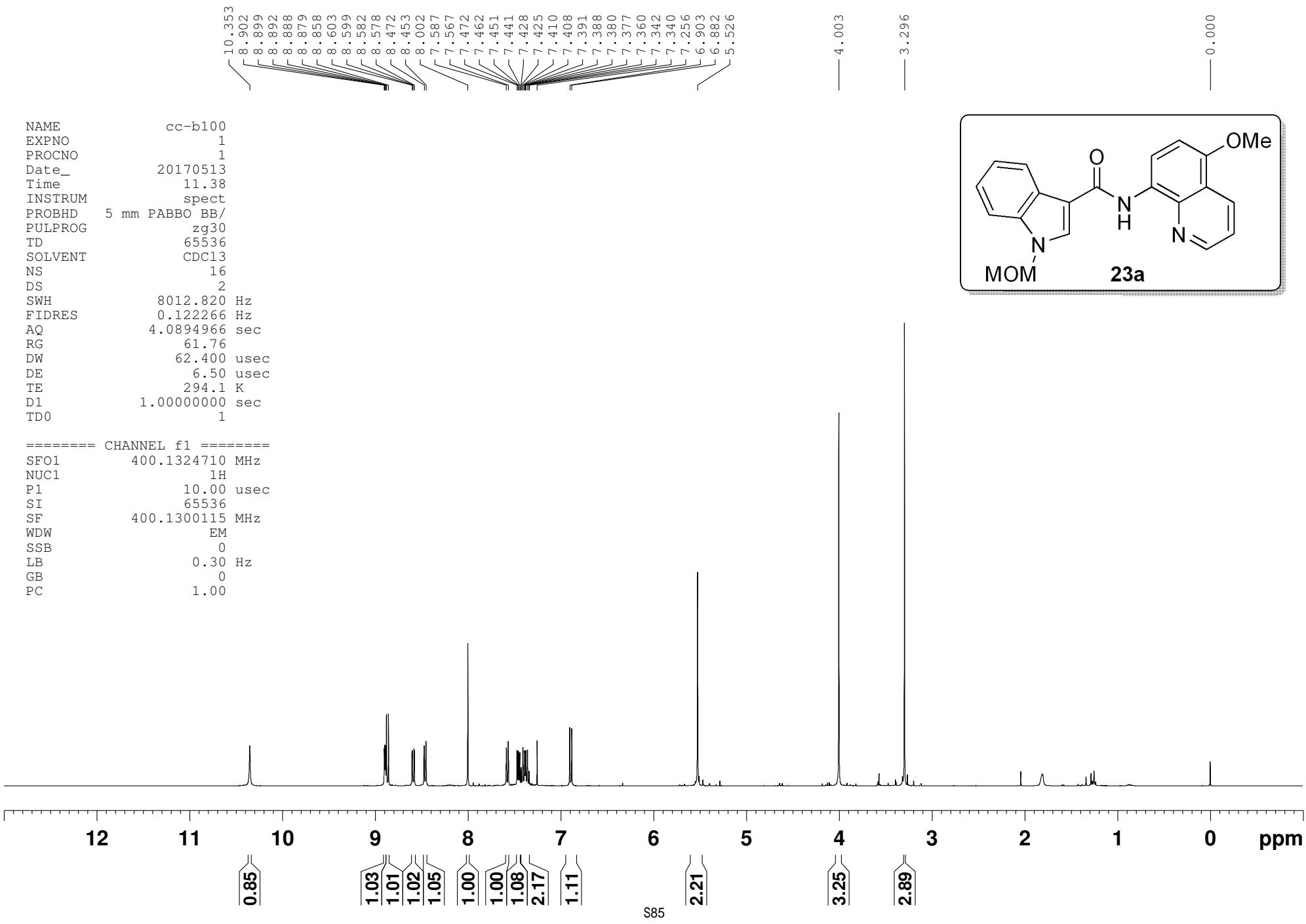


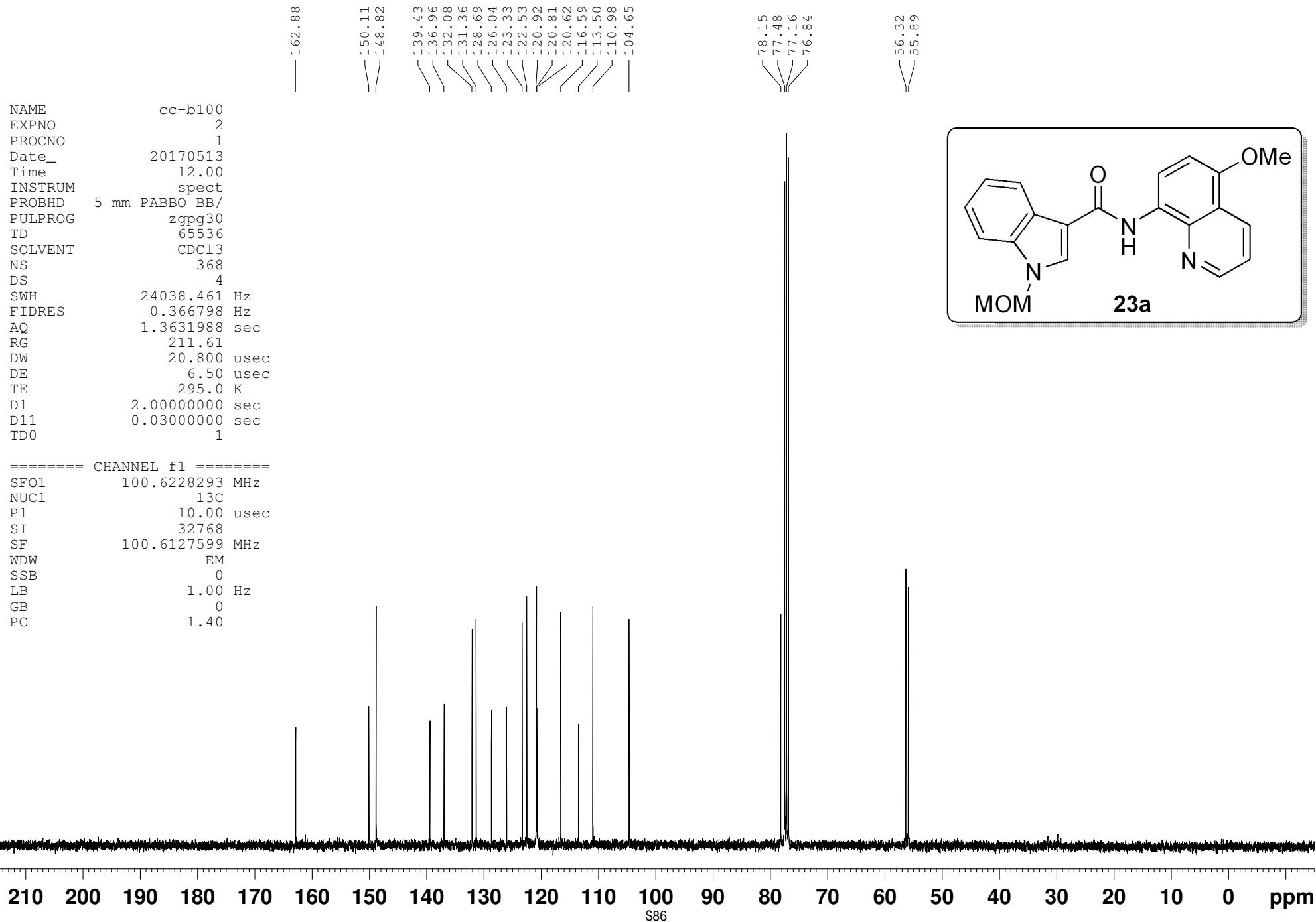


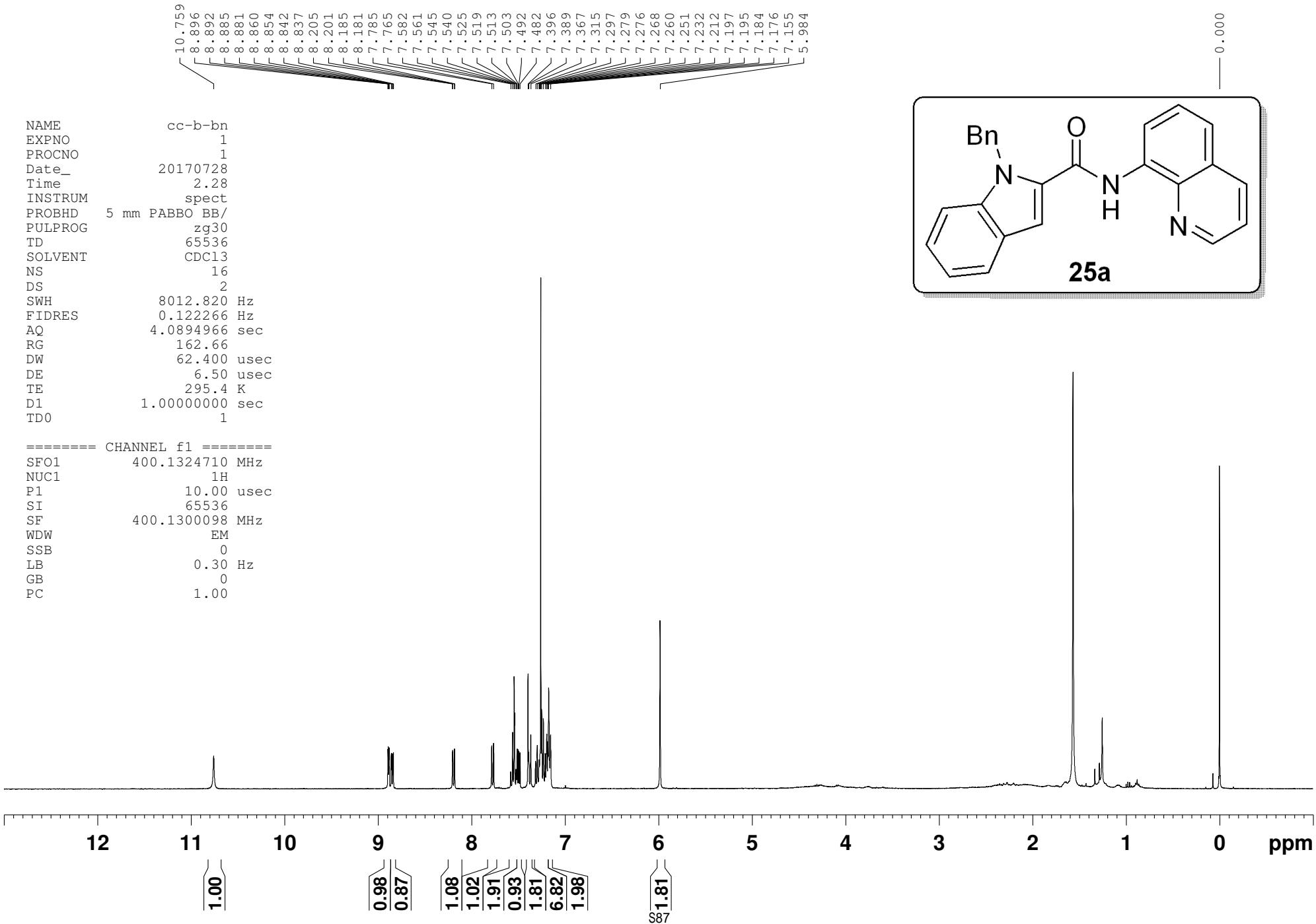


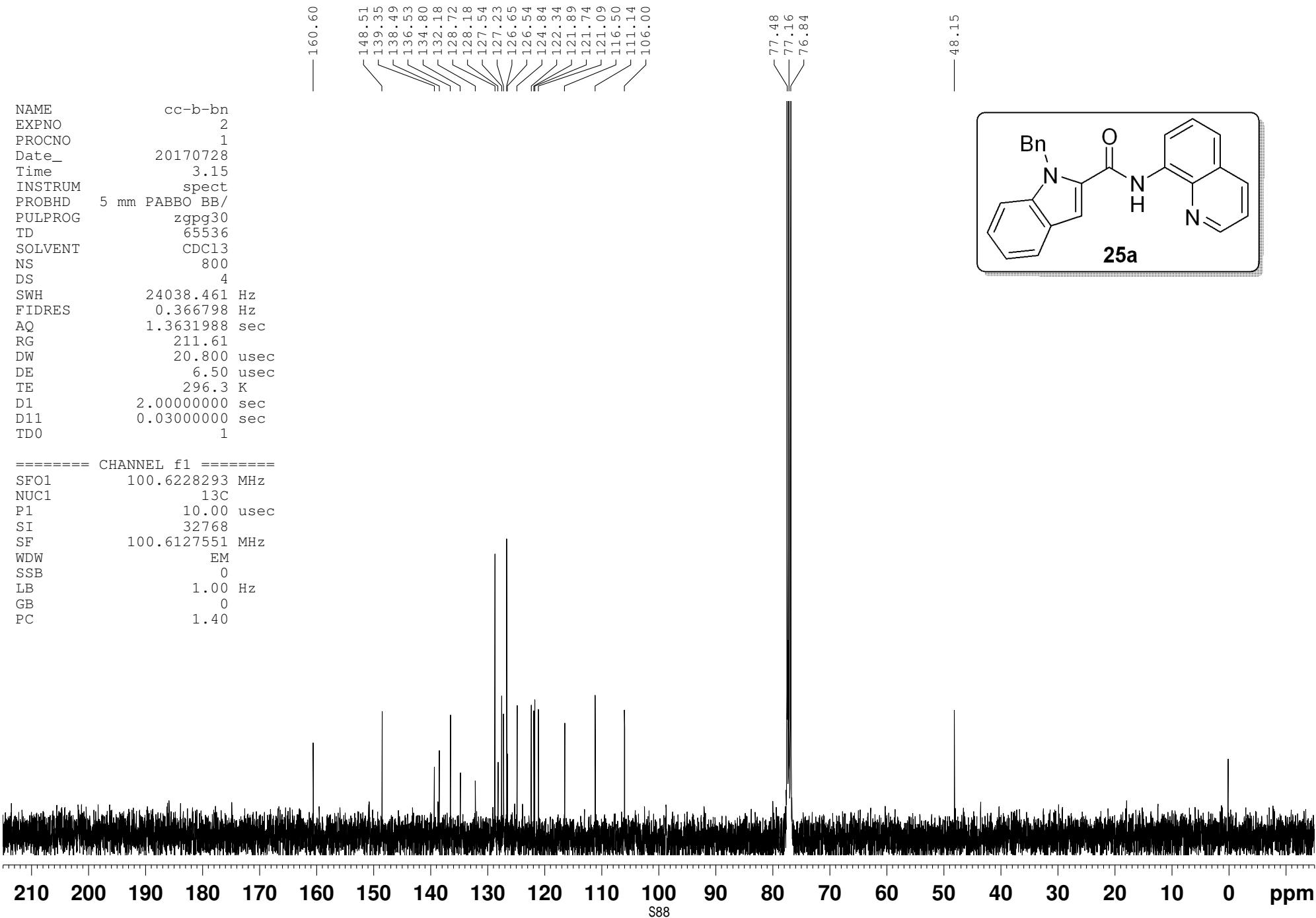


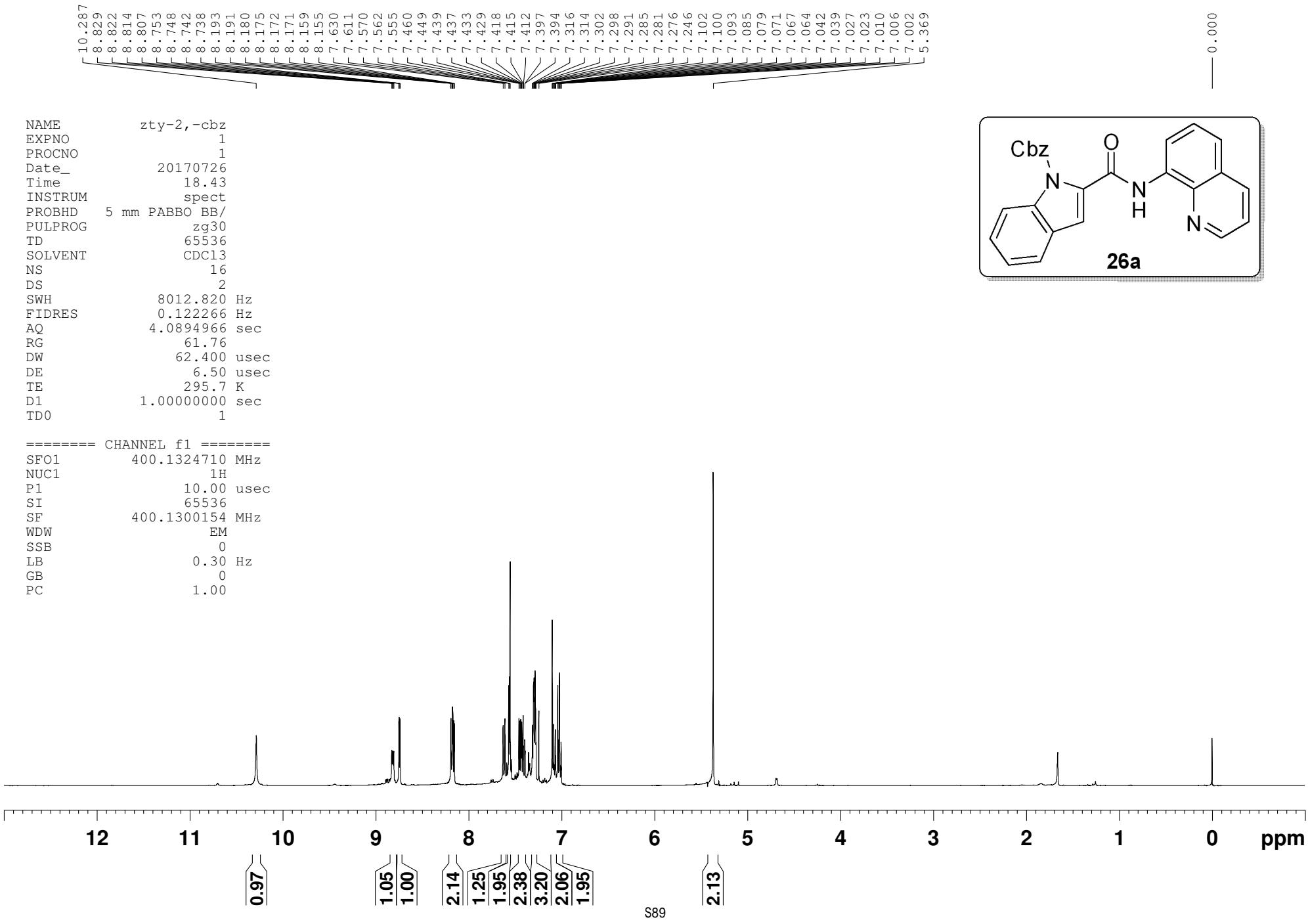






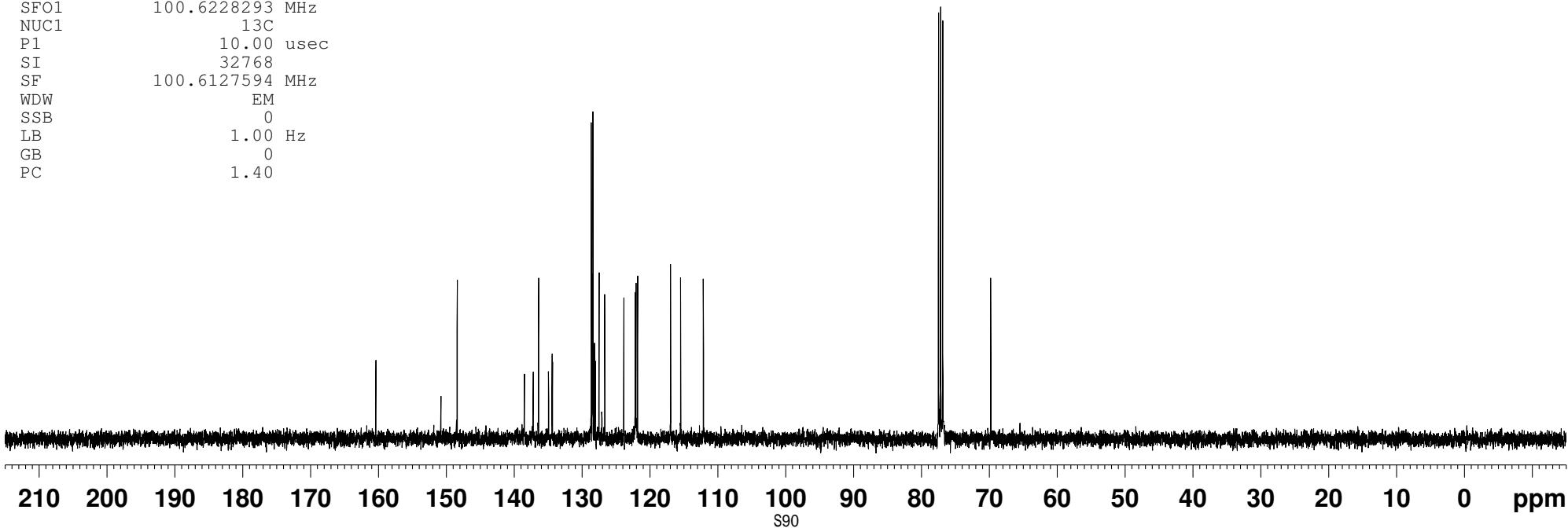
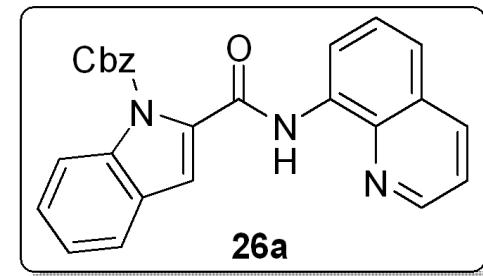
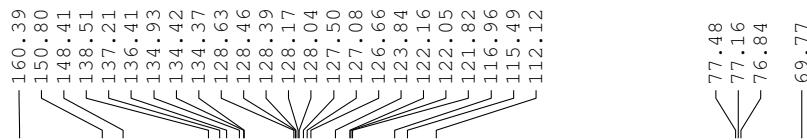


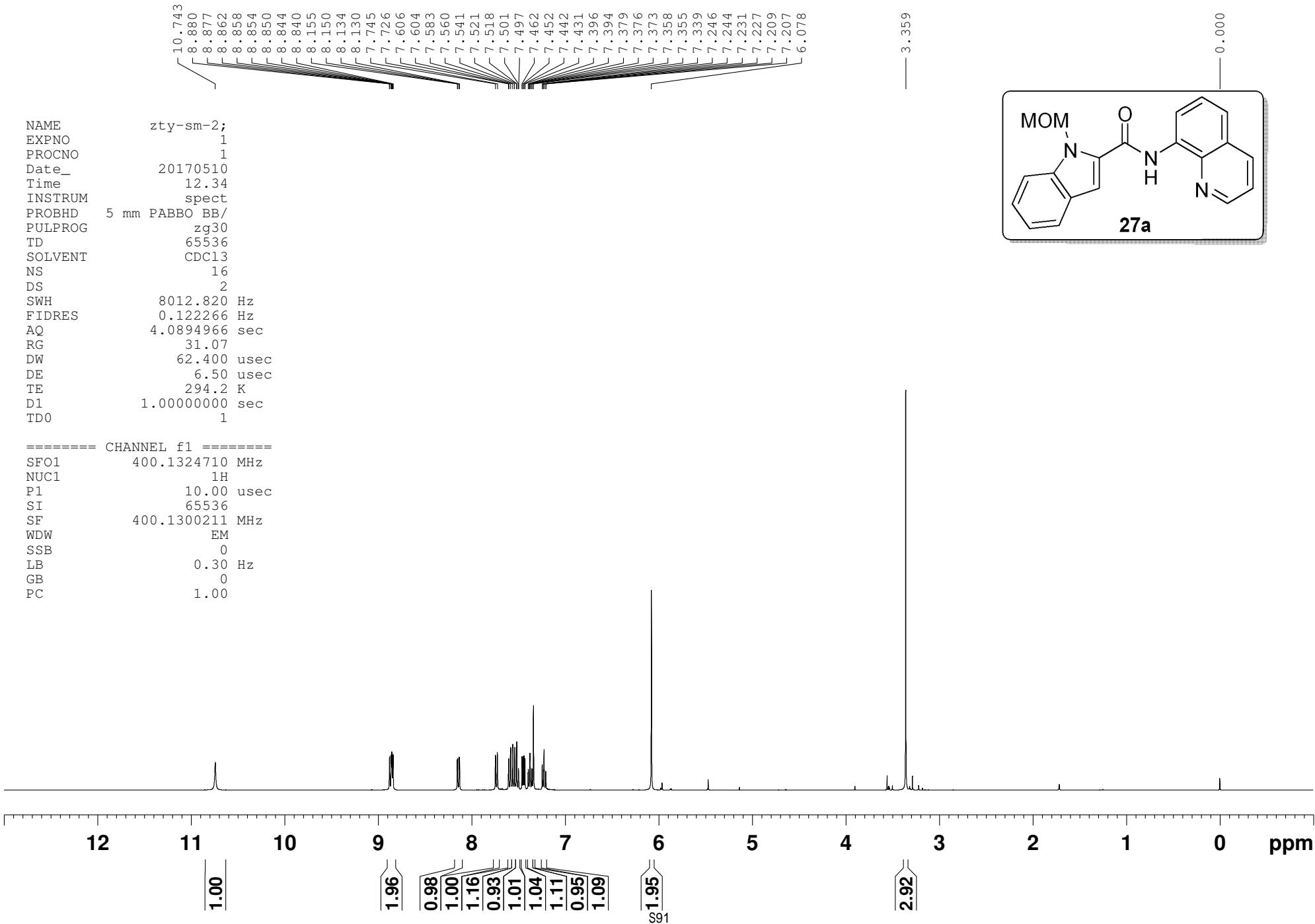




NAME zty-2,-cbz
 EXPNO 2
 PROCNO 1
 Date_ 20170726
 Time 19.06
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 71
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631988 sec
 RG 211.61
 DW 20.8000 usec
 DE 6.50 usec
 TE 296.7 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TDO 1

===== CHANNEL f1 =====
 SFO1 100.6228293 MHz
 NUC1 13C
 P1 10.00 usec
 SI 32768
 SF 100.6127594 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40





NAME zty-sm-2;
 EXPNO 2
 PROCNO 1
 Date_ 20170510
 Time 12.50
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 256
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631988 sec
 RG 211.61
 DW 20.800 usec
 DE 6.50 usec
 TE 294.9 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TDO 1

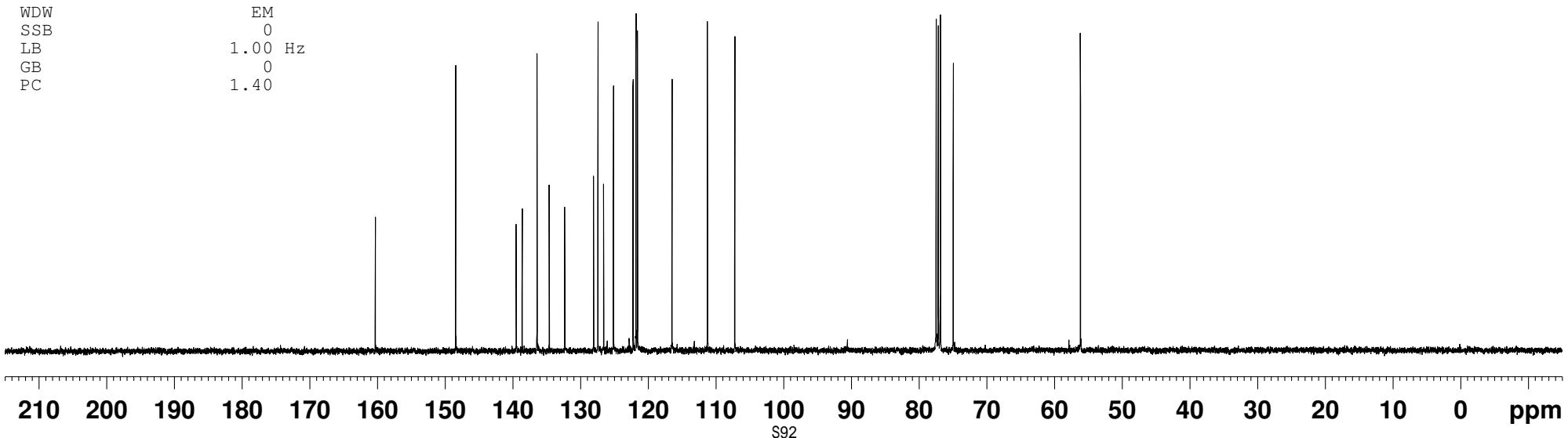
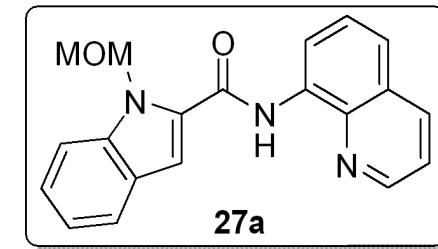
===== CHANNEL f1 =====
 SFO1 100.6228293 MHz
 NUC1 13C
 P1 10.00 usec
 SI 32768
 SF 100.6127641 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

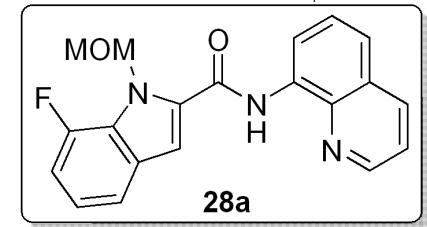
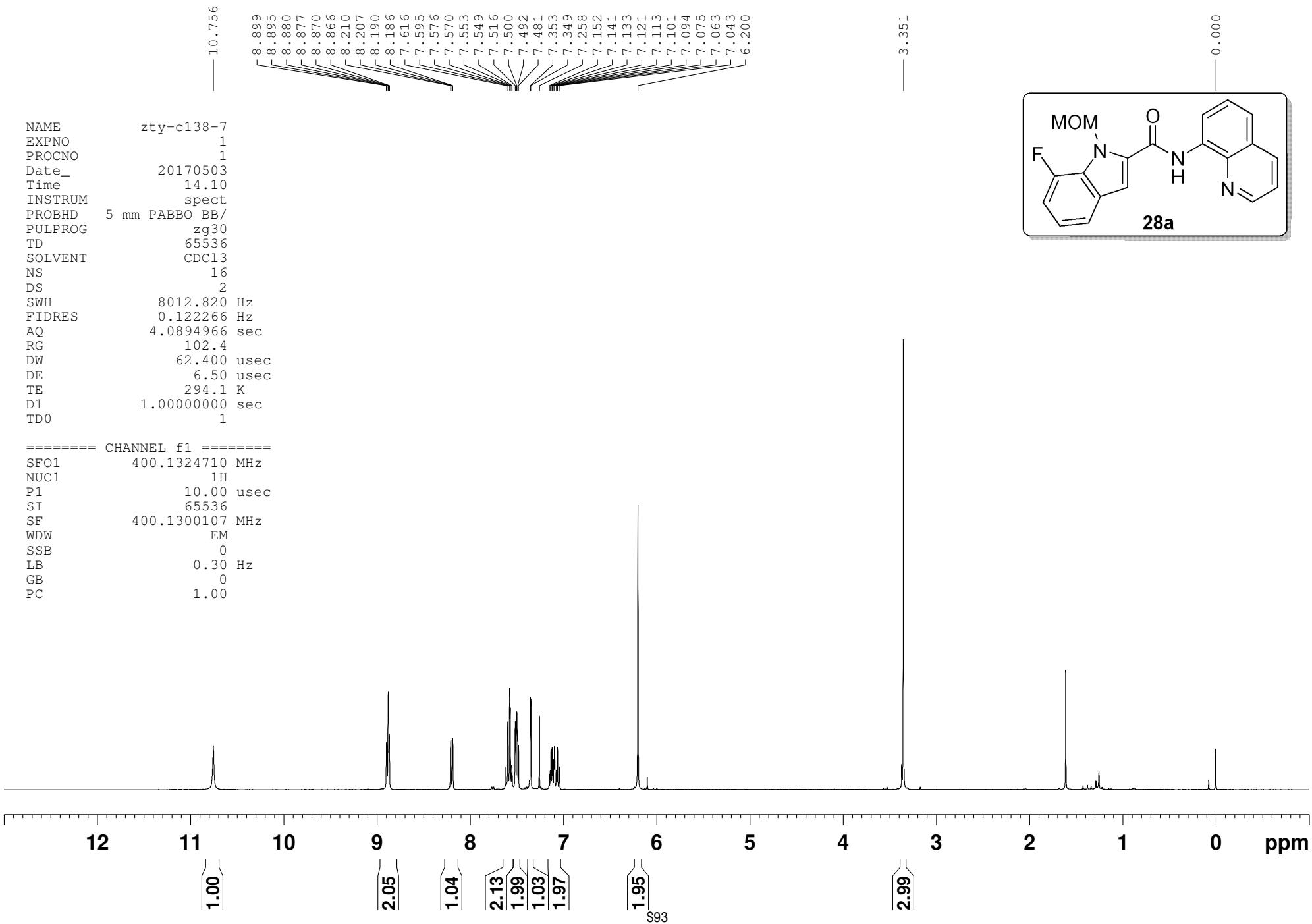
— 160.33 —

148.46
 139.54
 138.64
 136.45
 134.65
 132.34
 128.09
 127.45
 126.60
 125.16
 122.26
 121.84
 121.82
 121.60
 116.50
 111.26
 107.23

77.48
 77.16
 76.84
 74.95

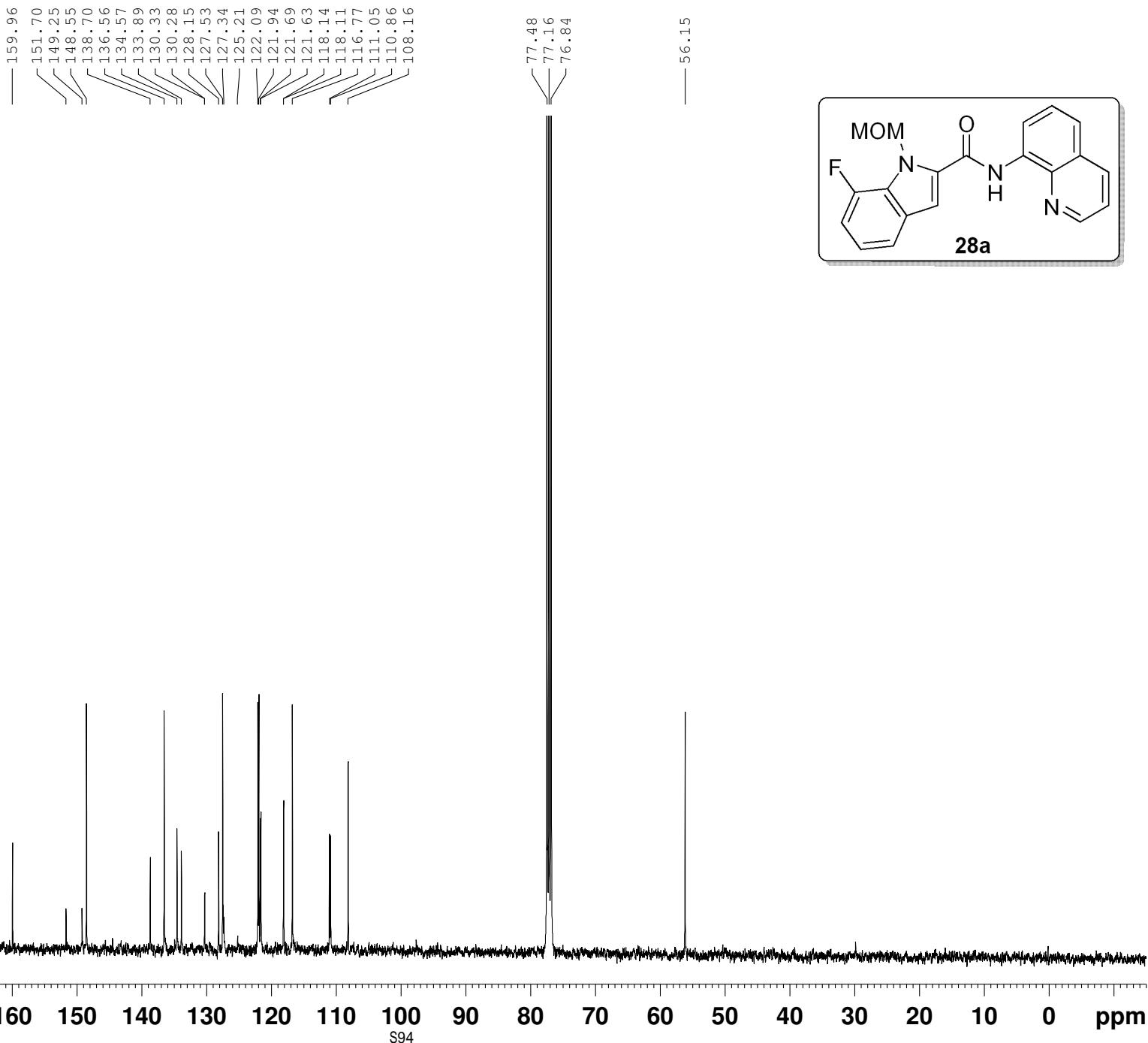
— 56.16 —

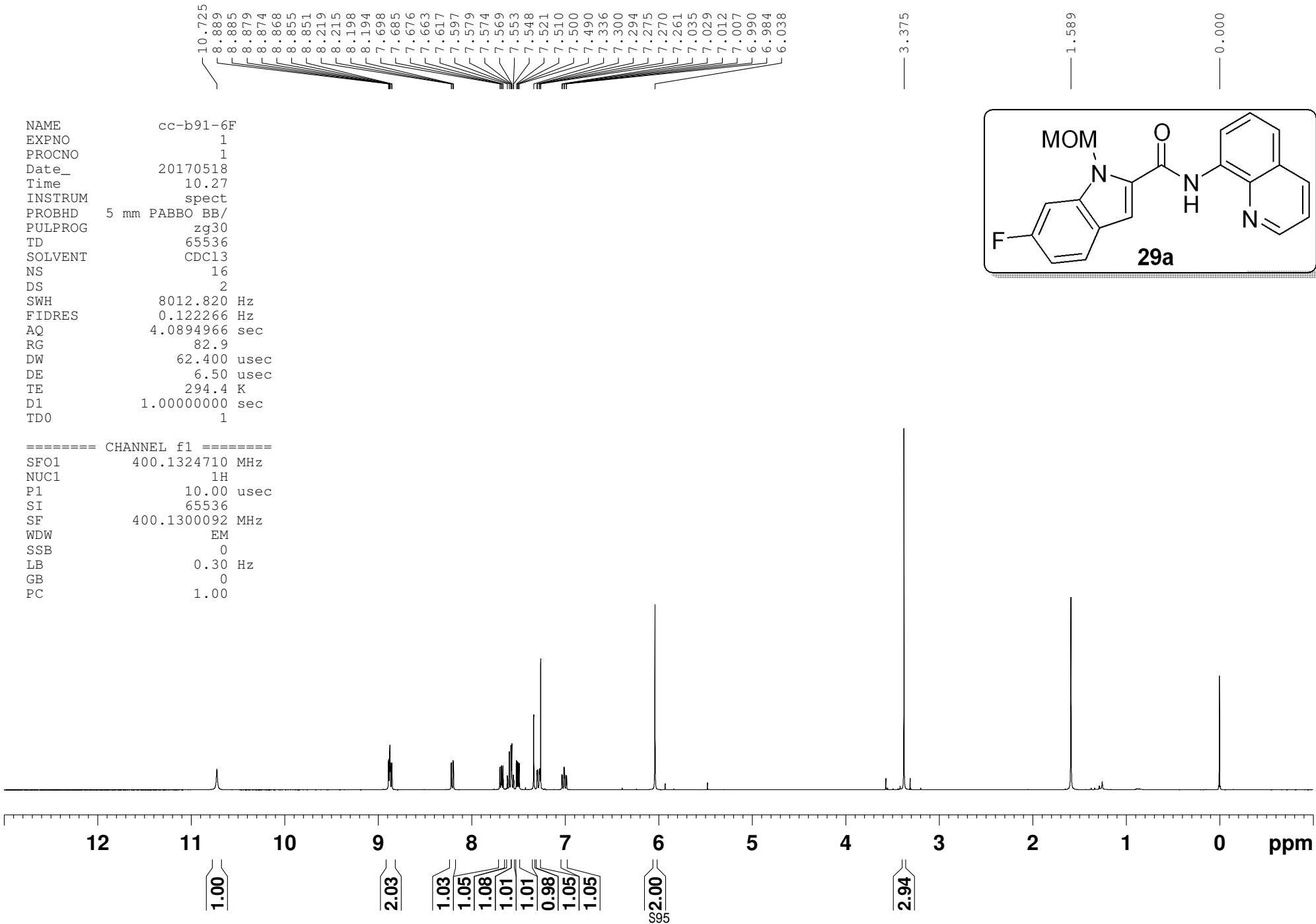


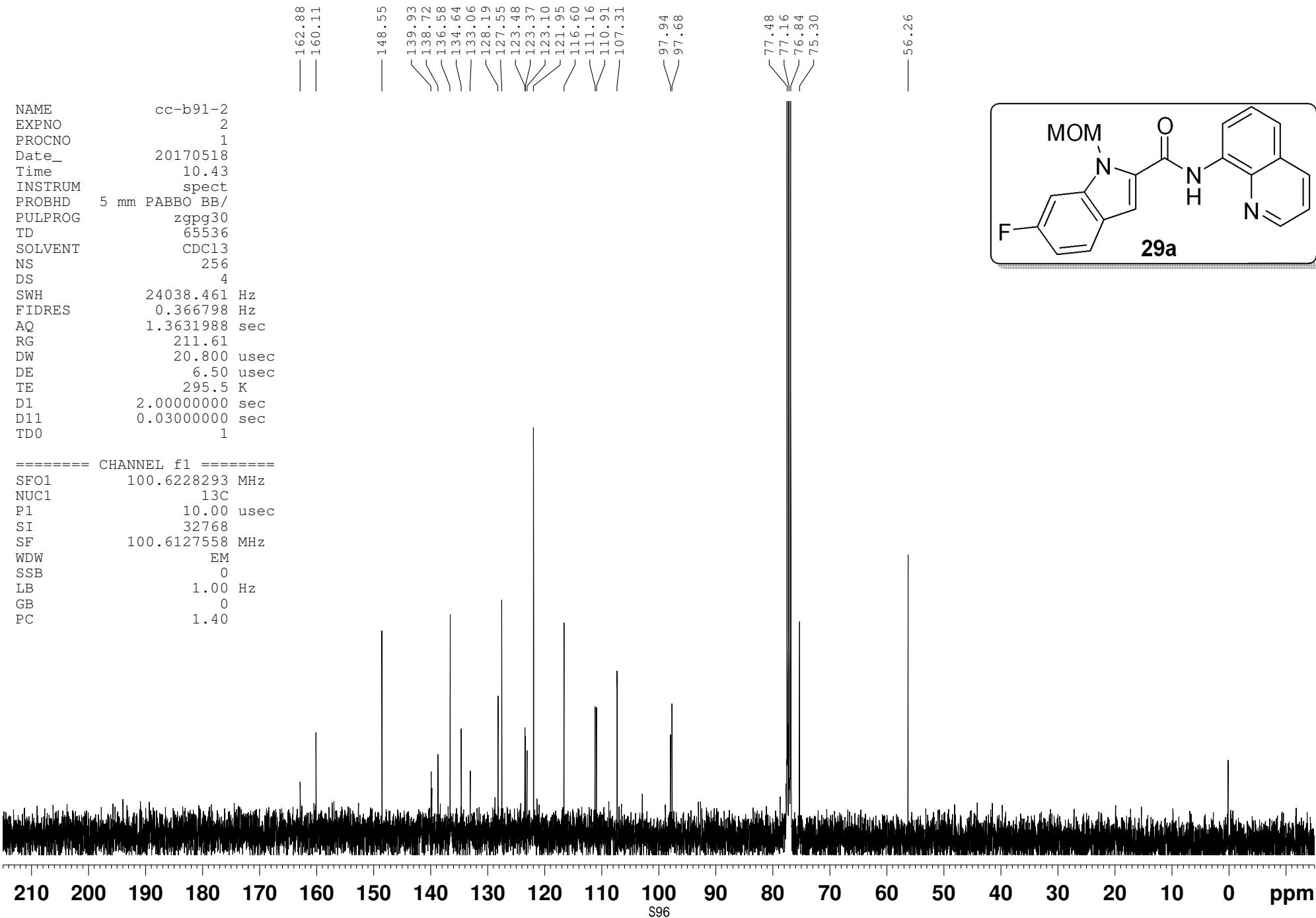


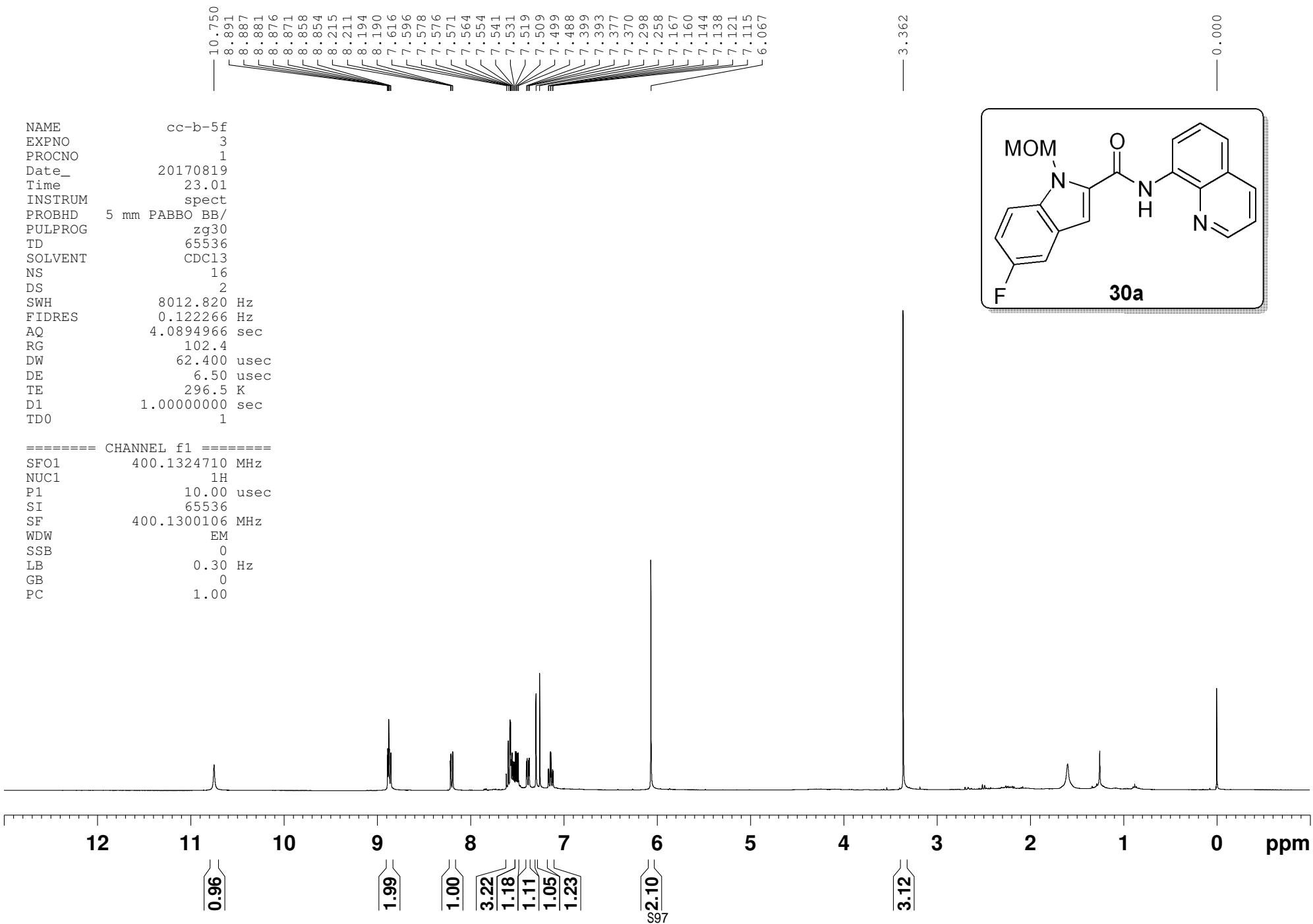
NAME zty-c138-7
 EXPNO 2
 PROCNO 1
 Date_ 20170503
 Time 14.30
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 1024
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631988 sec
 RG 211.61
 DW 20.800 usec
 DE 6.50 usec
 TE 294.9 K
 D1 2.0000000 sec
 D11 0.03000000 sec
 TDO 1

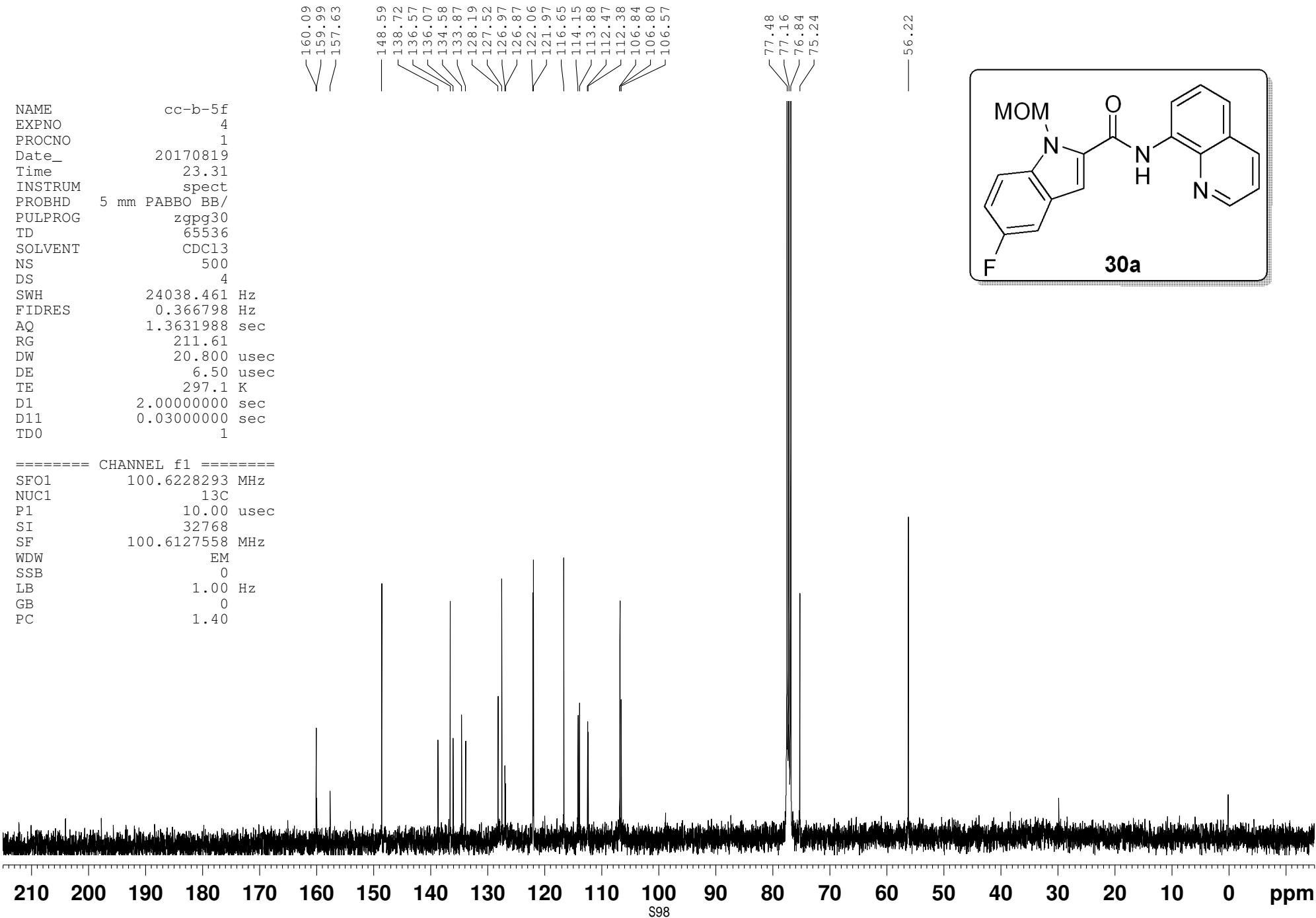
===== CHANNEL f1 =====
 SFO1 100.6228293 MHz
 NUC1 13C
 P1 10.00 usec
 SI 32768
 SF 100.6127570 MHz
 WDW EM
 SSB 0
 LB 3.00 Hz
 GB 0
 PC 1.40

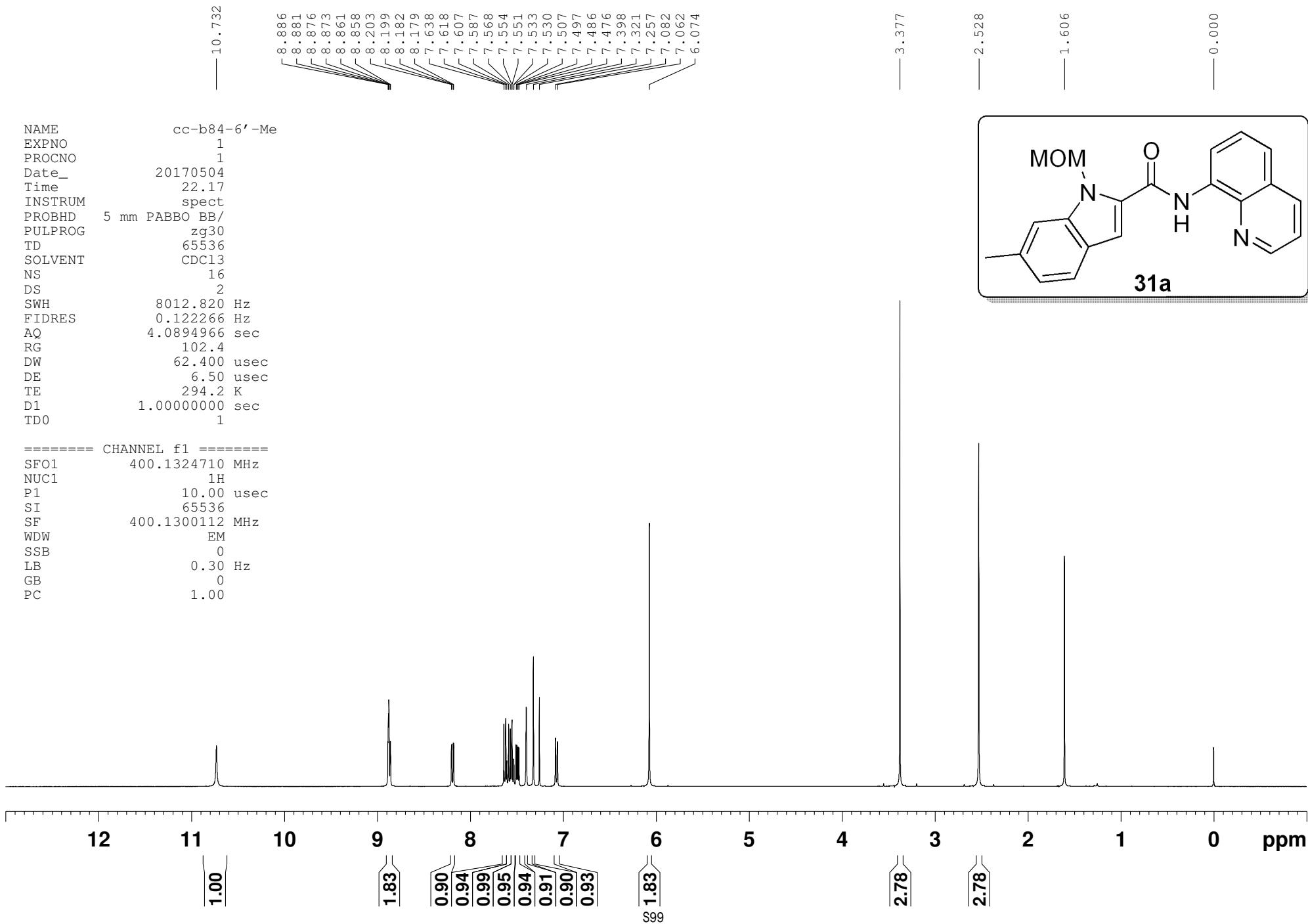






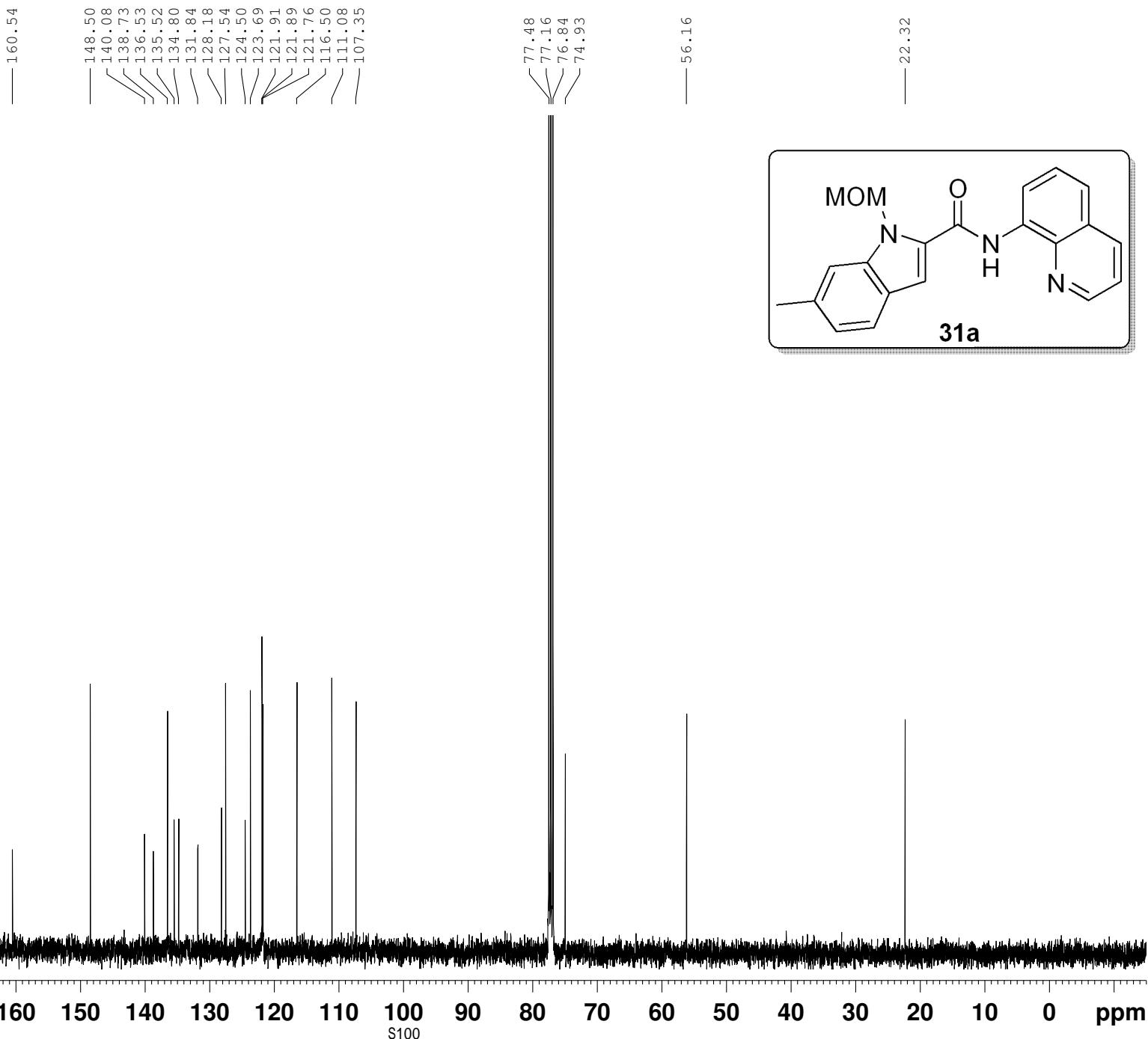


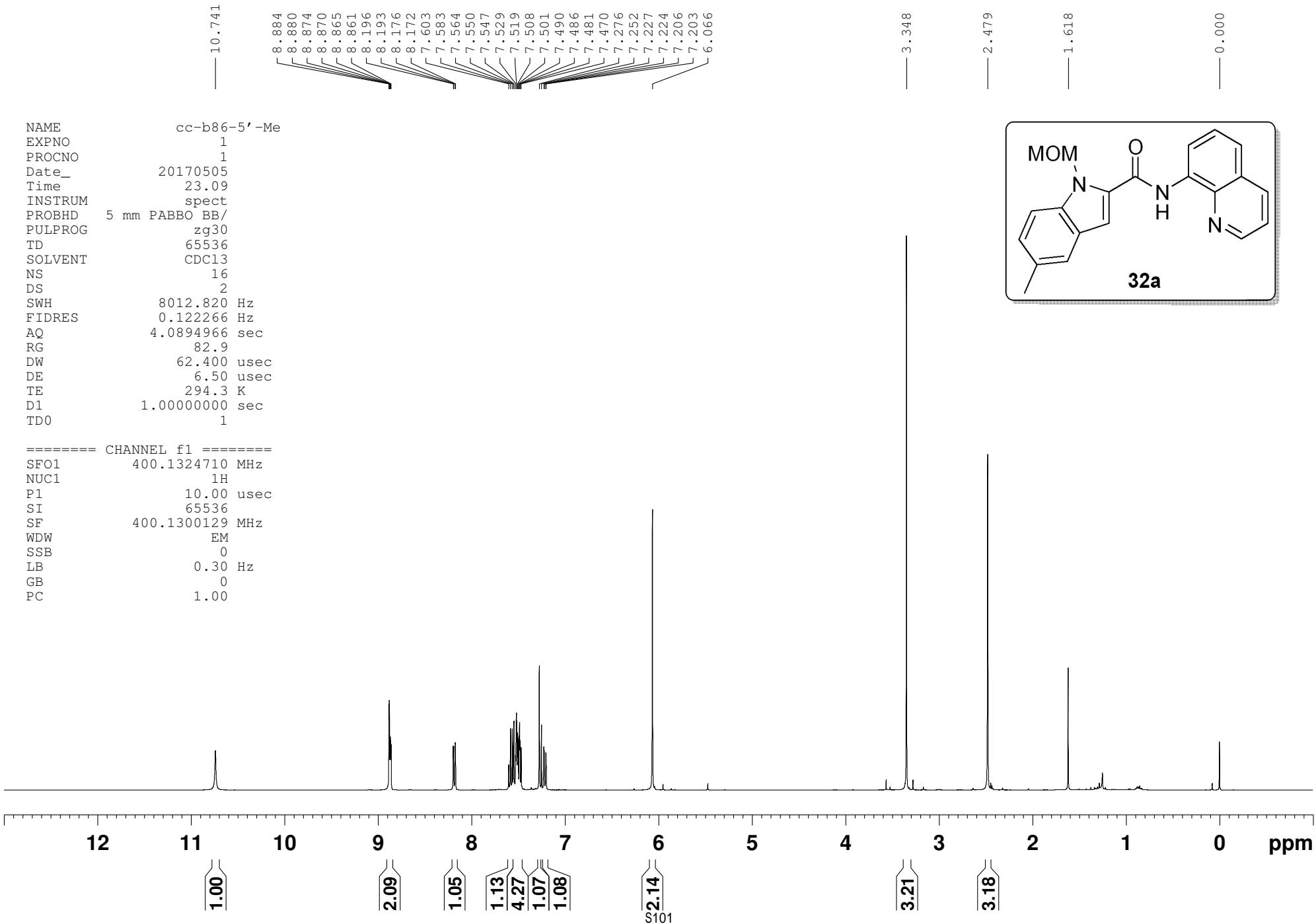


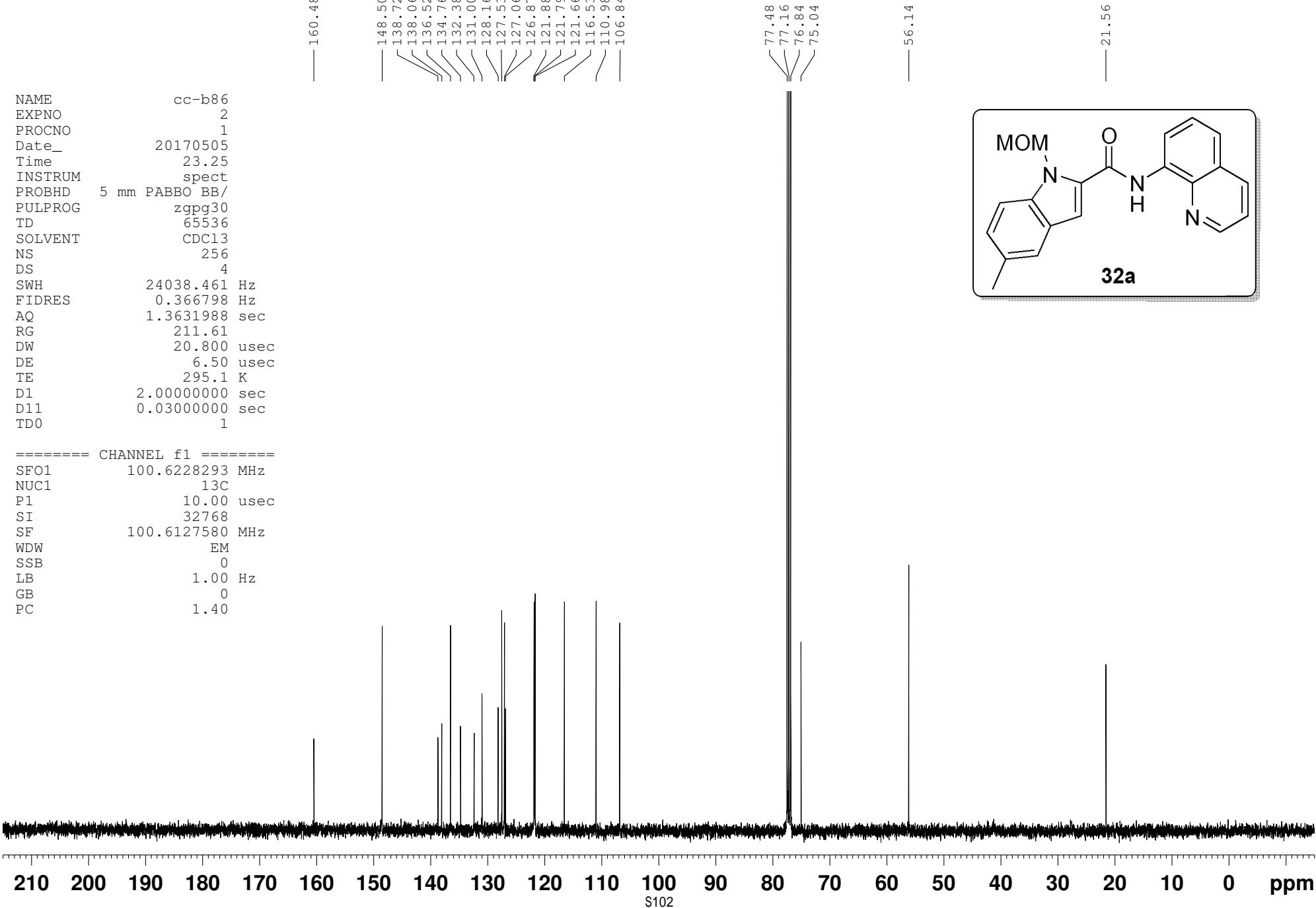


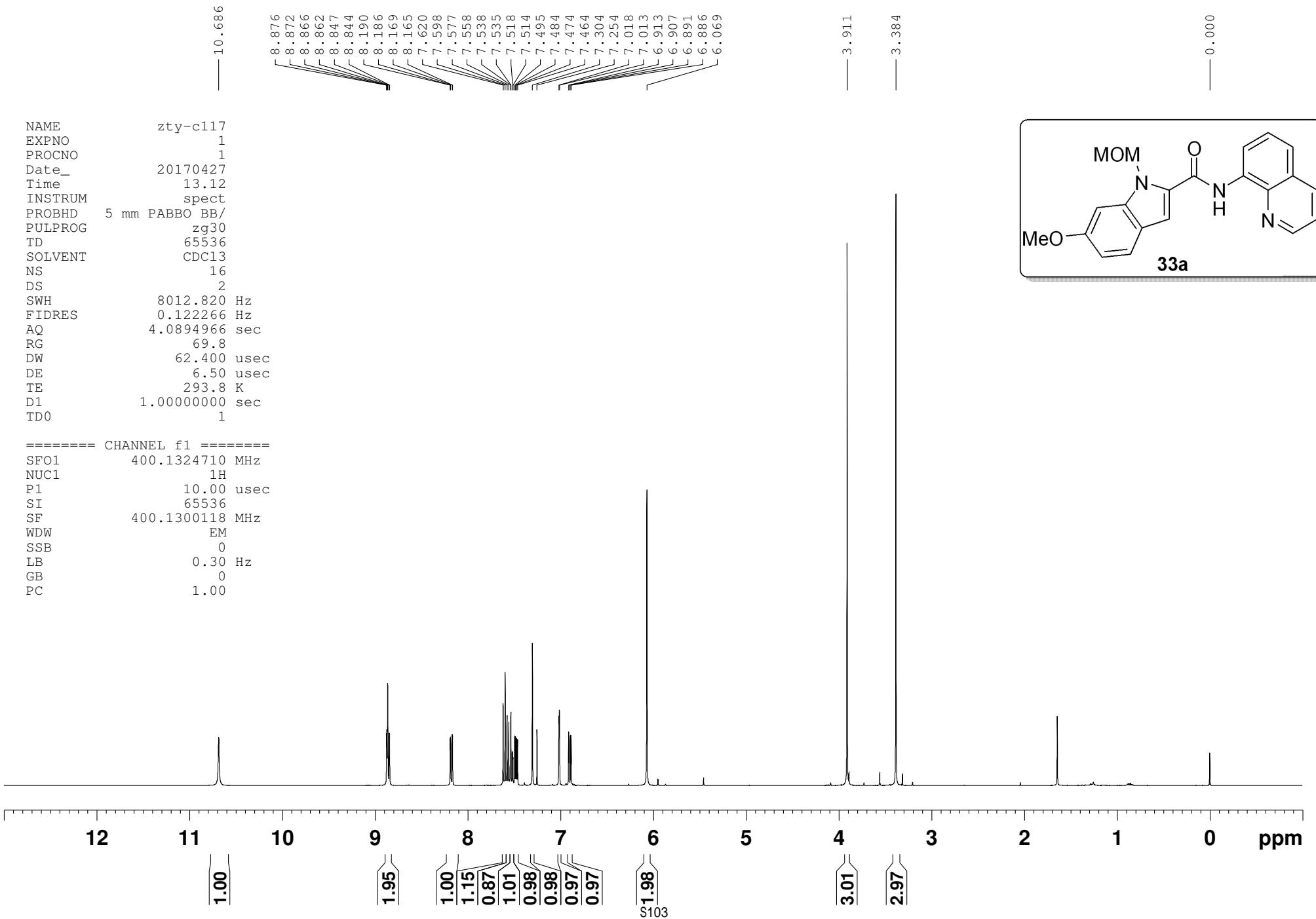
NAME cc-b84
 EXPNO 2
 PROCNO 1
 Date_ 20170504
 Time 22.32
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 256
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631988 sec
 RG 211.61
 DW 20.800 usec
 DE 6.50 usec
 TE 295.1 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TDO 1

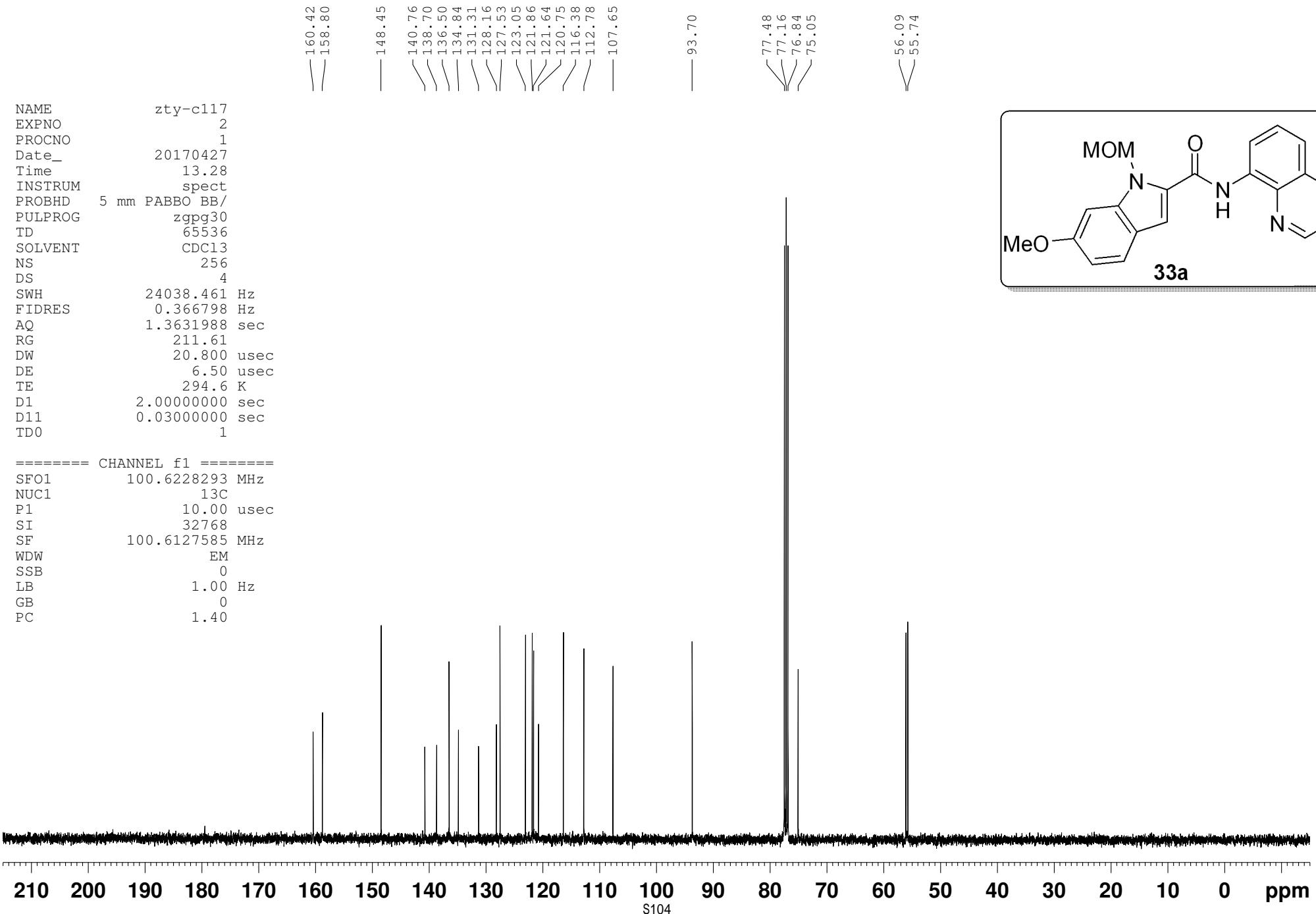
===== CHANNEL f1 =====
 SFO1 100.6228293 MHz
 NUC1 13C
 P1 10.00 usec
 SI 32768
 SF 100.6127570 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

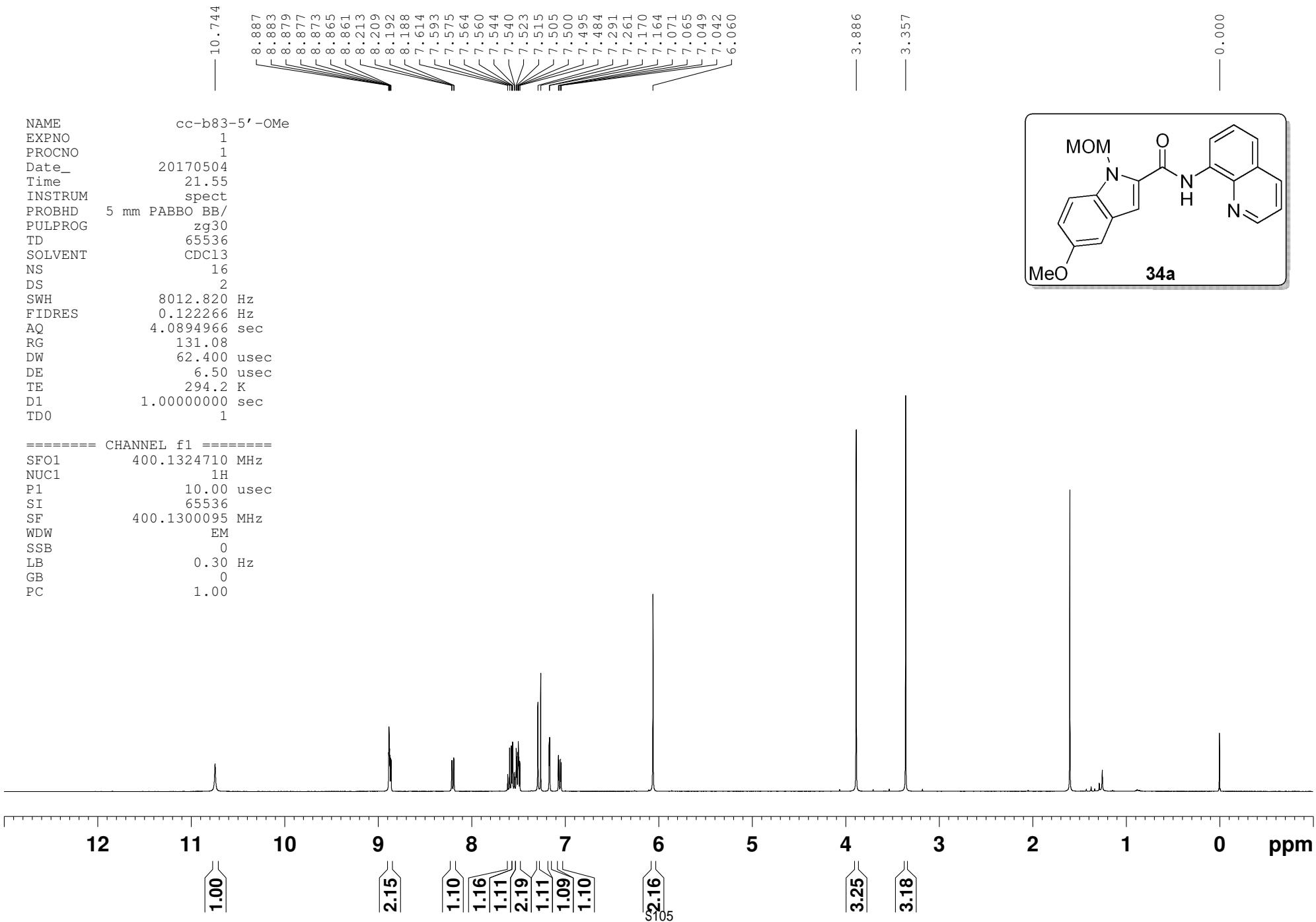


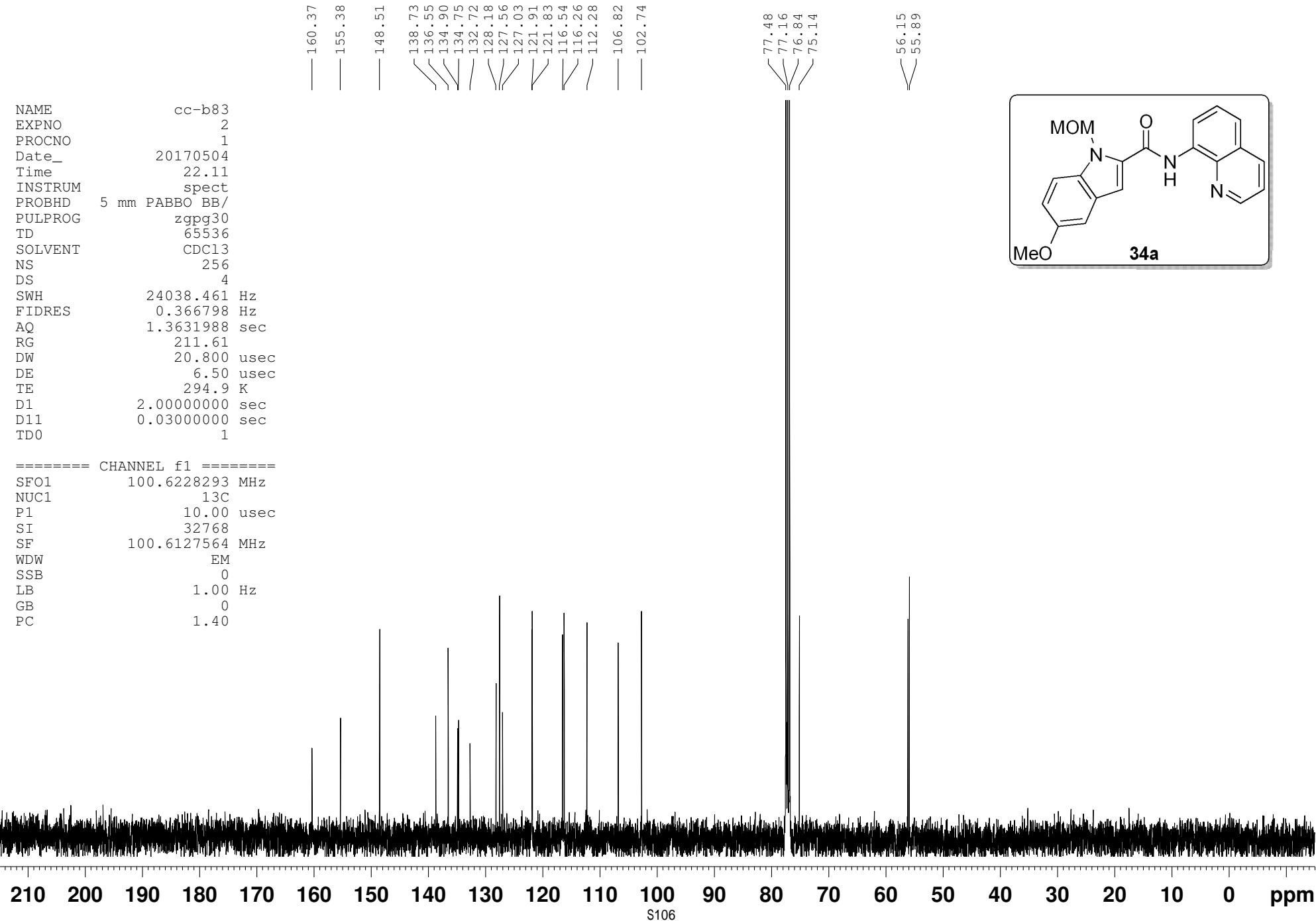


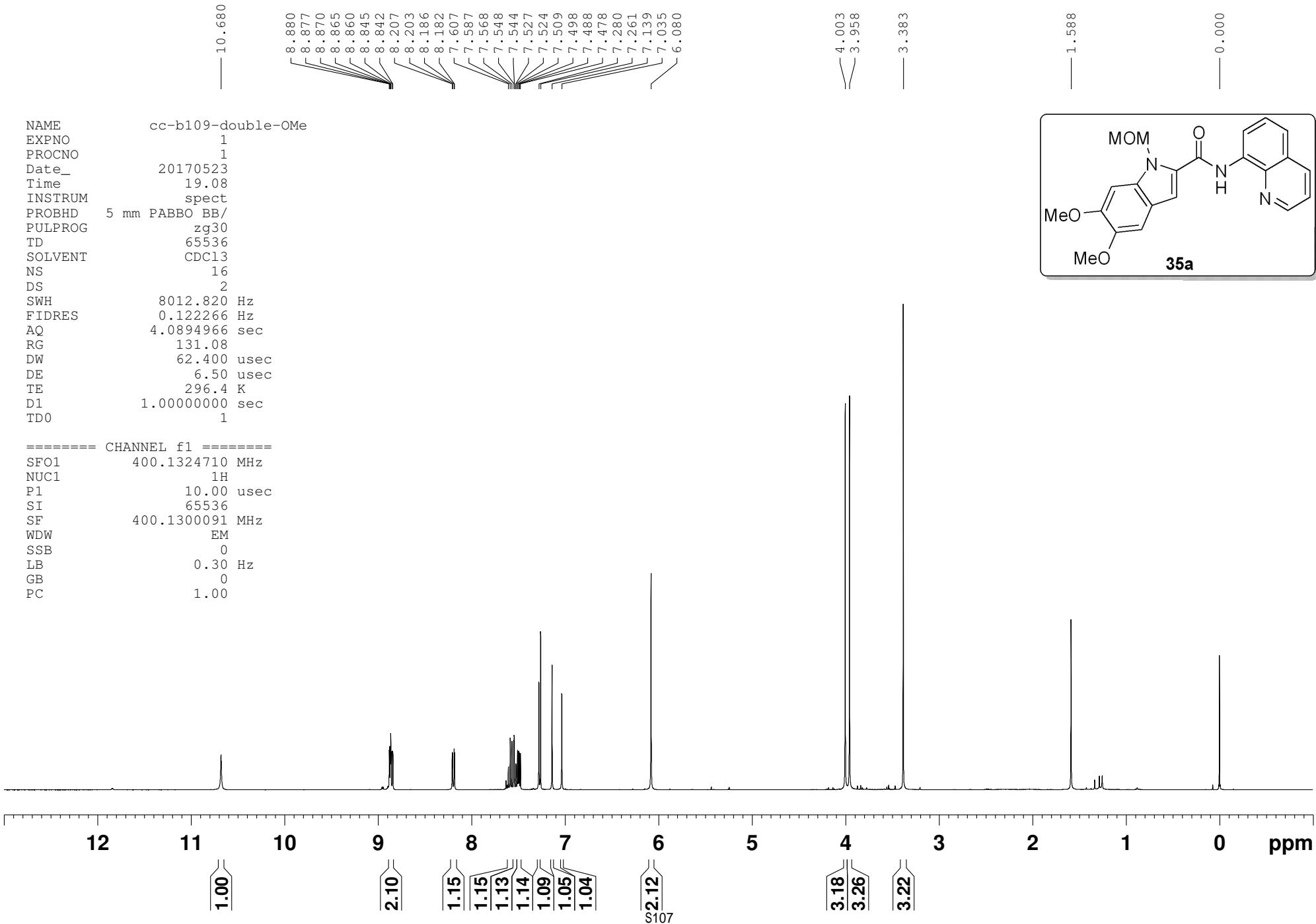


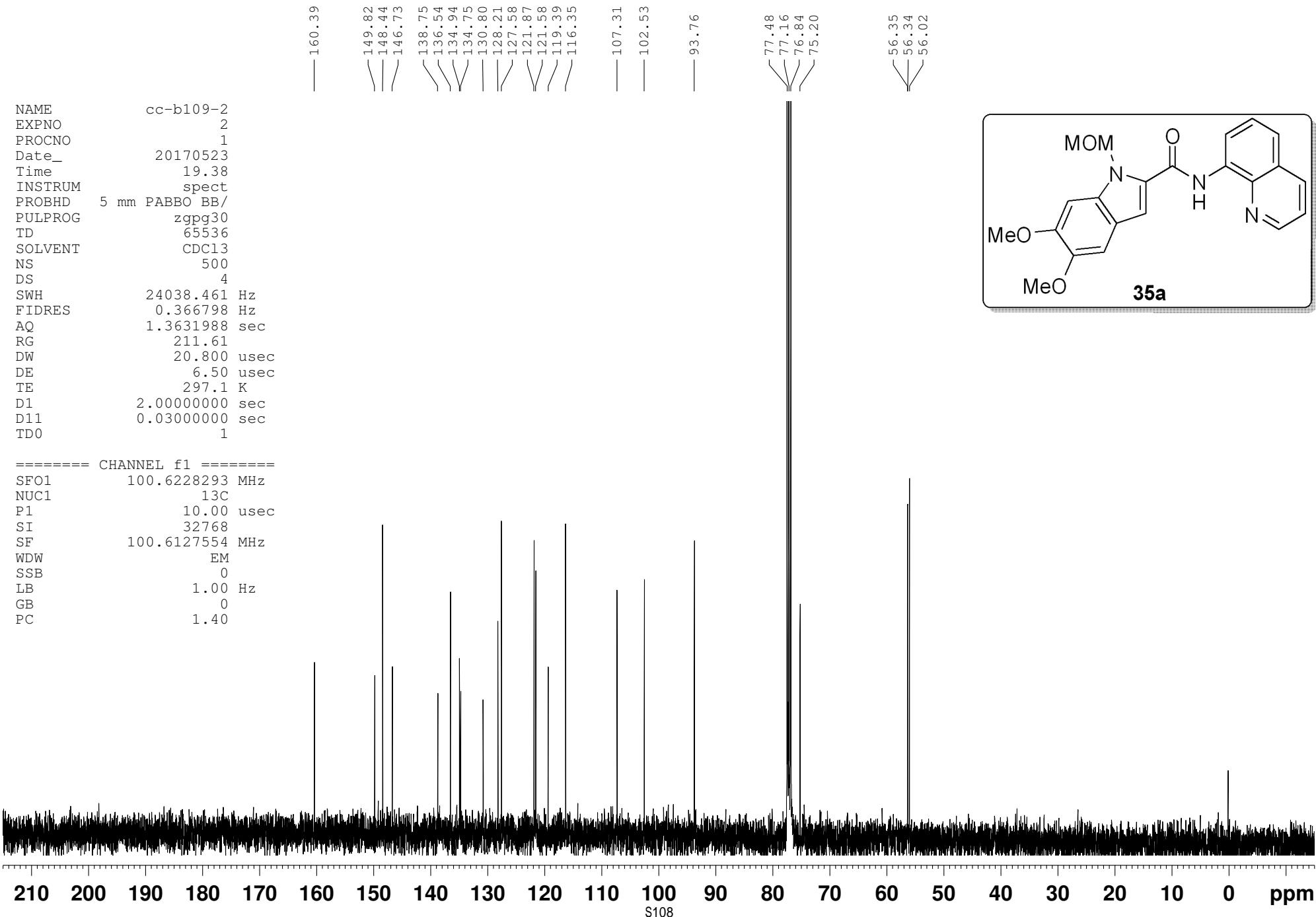


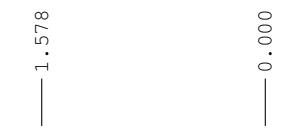
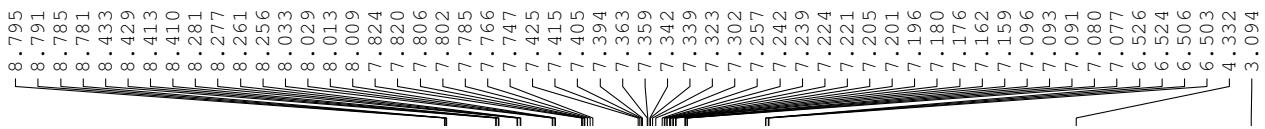






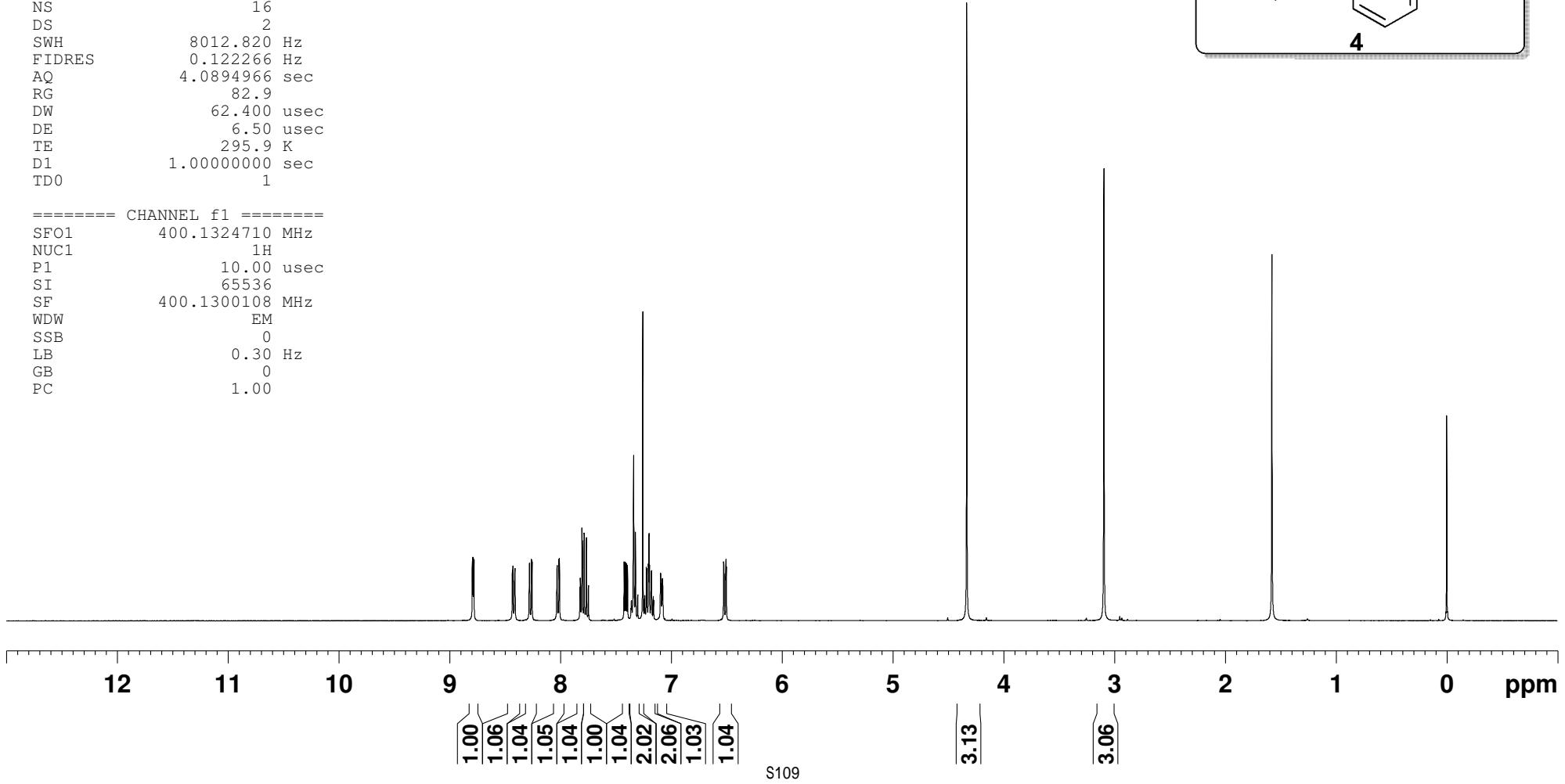
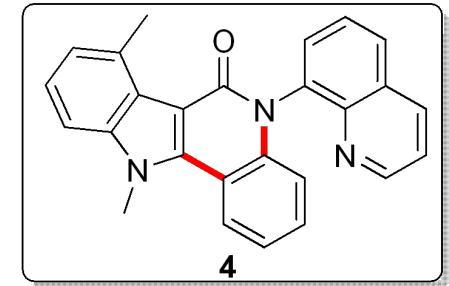






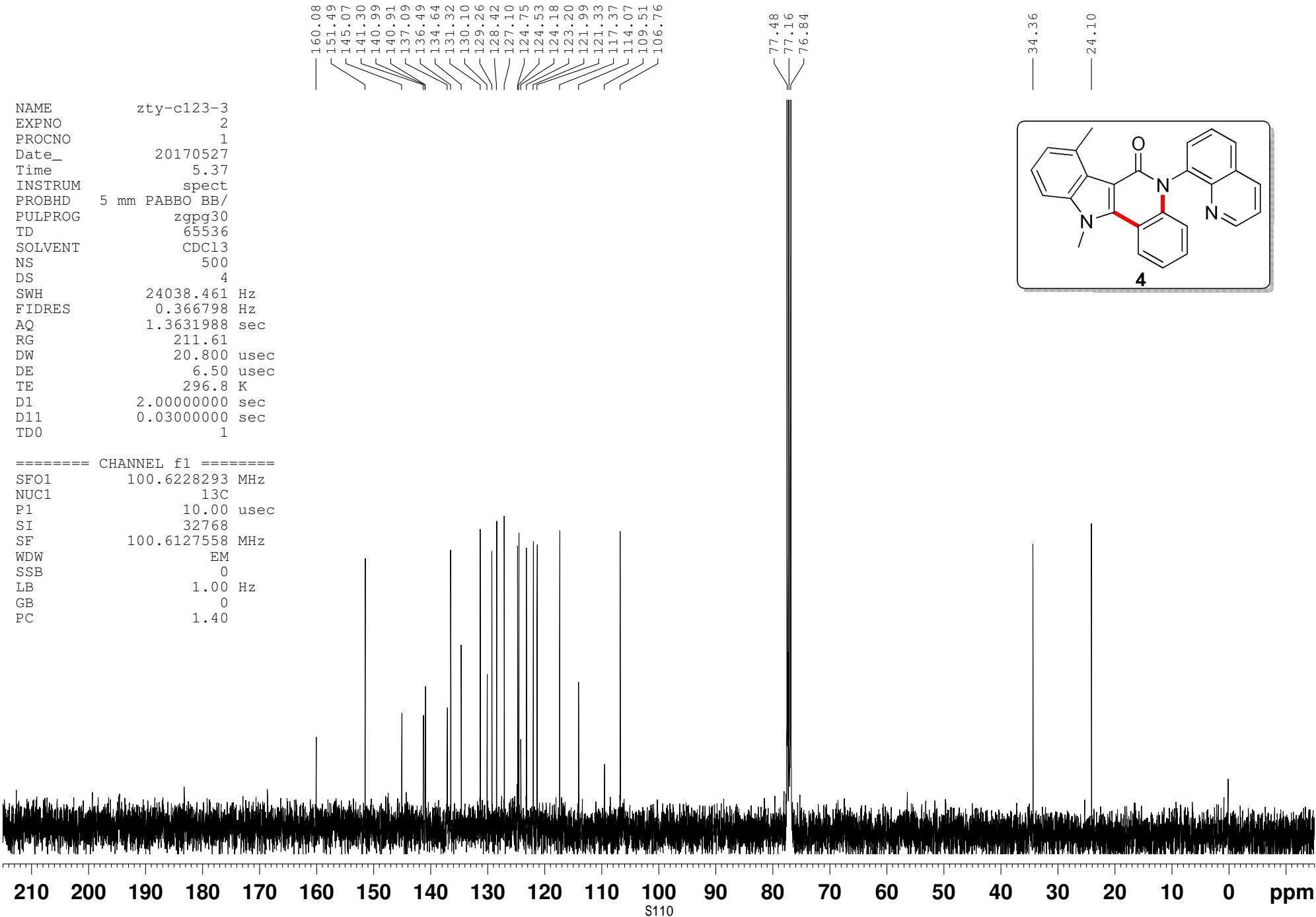
NAME zty-c123-3
 EXPNO 1
 PROCNO 1
 Date_ 20170527
 Time 5.07
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 8012.820 Hz
 FIDRES 0.122266 Hz
 AQ 4.0894966 sec
 RG 82.9
 DW 62.400 usec
 DE 6.50 usec
 TE 295.9 K
 D1 1.0000000 sec
 TDO 1

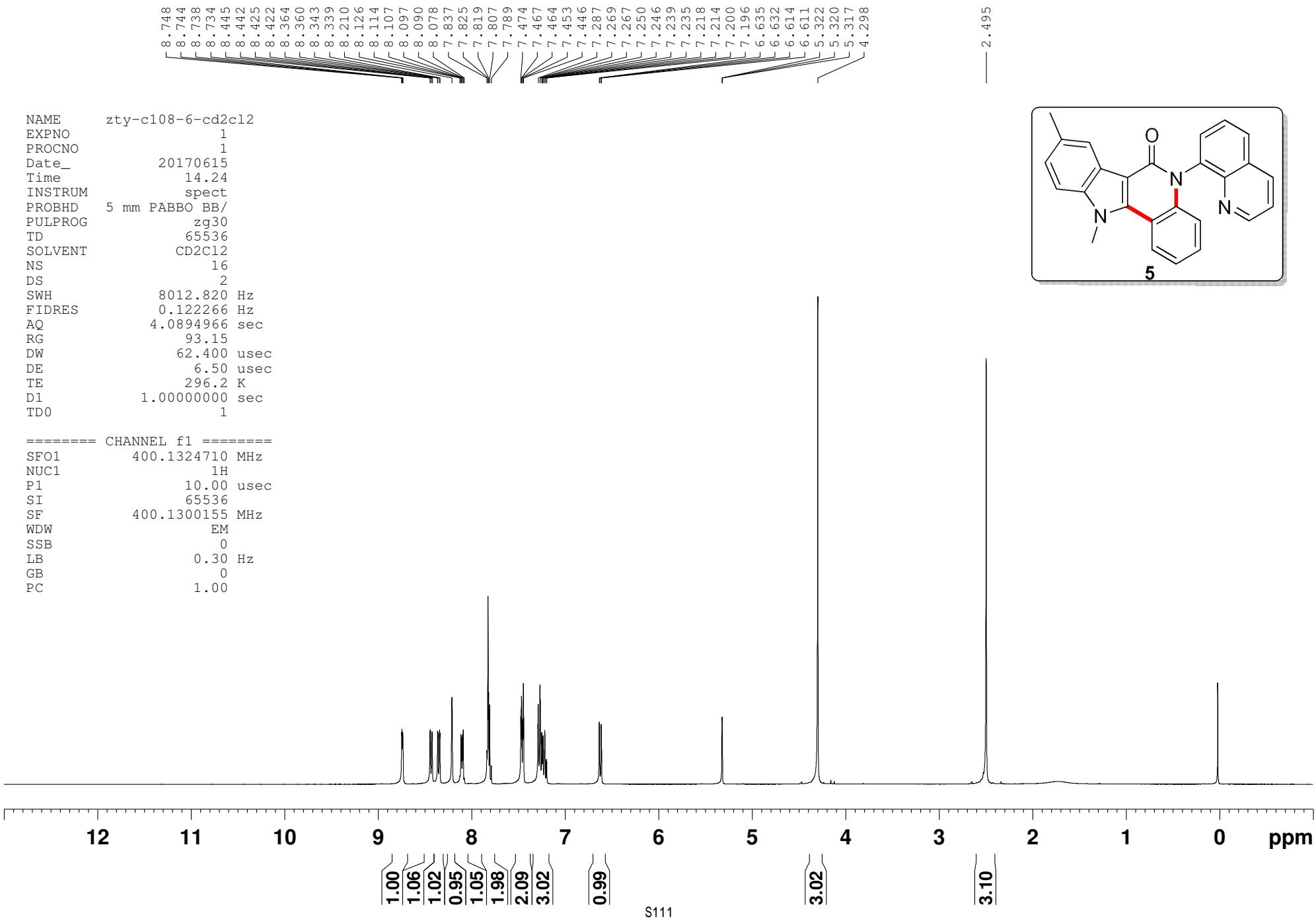
===== CHANNEL f1 =====
 SFO1 400.1324710 MHz
 NUC1 1H
 P1 10.00 usec
 SI 65536
 SF 400.1300108 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



NAME zty-c123-3
 EXPNO 2
 PROCNO 1
 Date_ 20170527
 Time 5.37
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 500
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631988 sec
 RG 211.61
 DW 20.800 usec
 DE 6.50 usec
 TE 296.8 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TDO 1

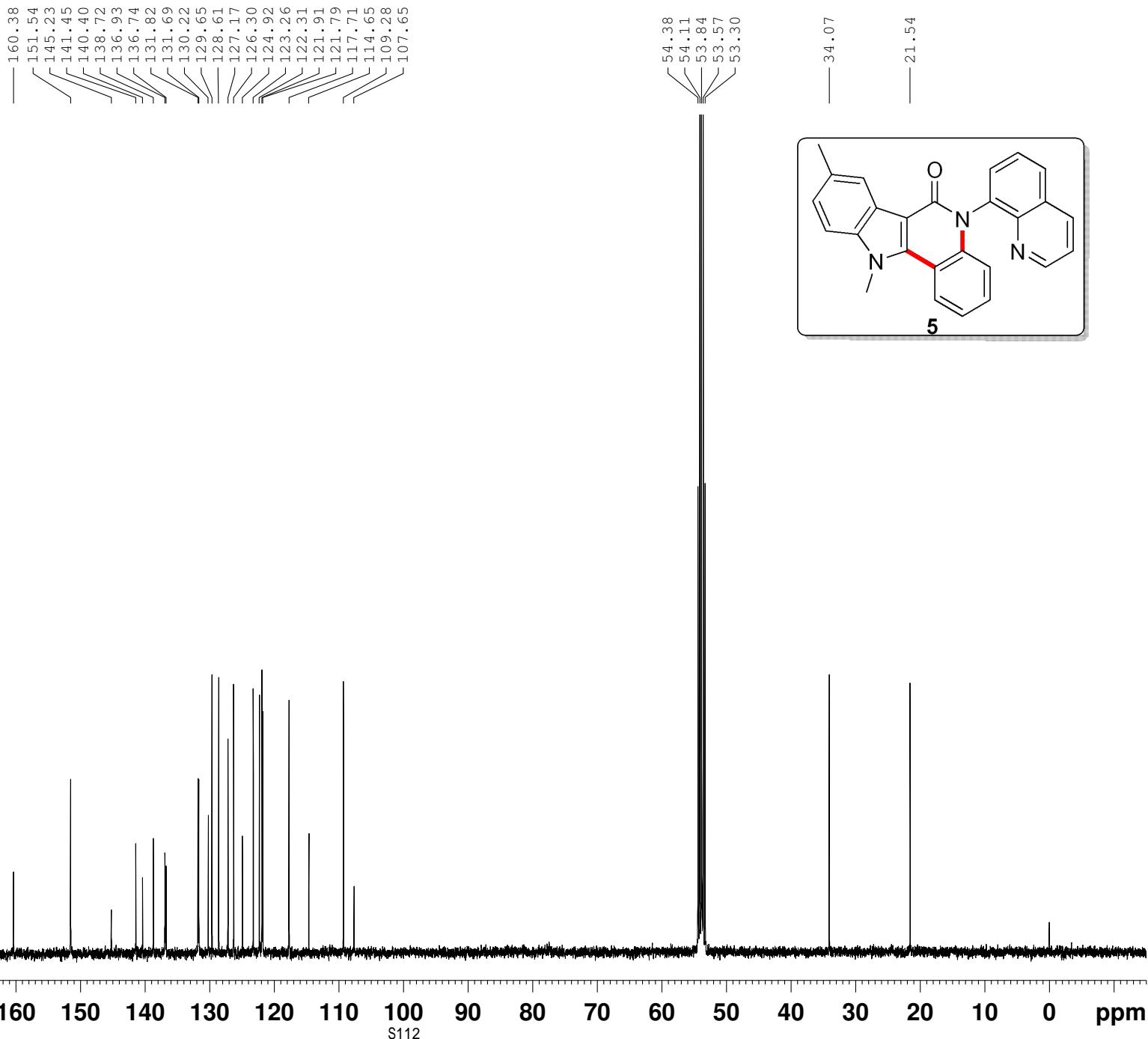
===== CHANNEL f1 =====
 SFO1 100.6228293 MHz
 NUC1 13C
 P1 10.00 usec
 SI 32768
 SF 100.6127558 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

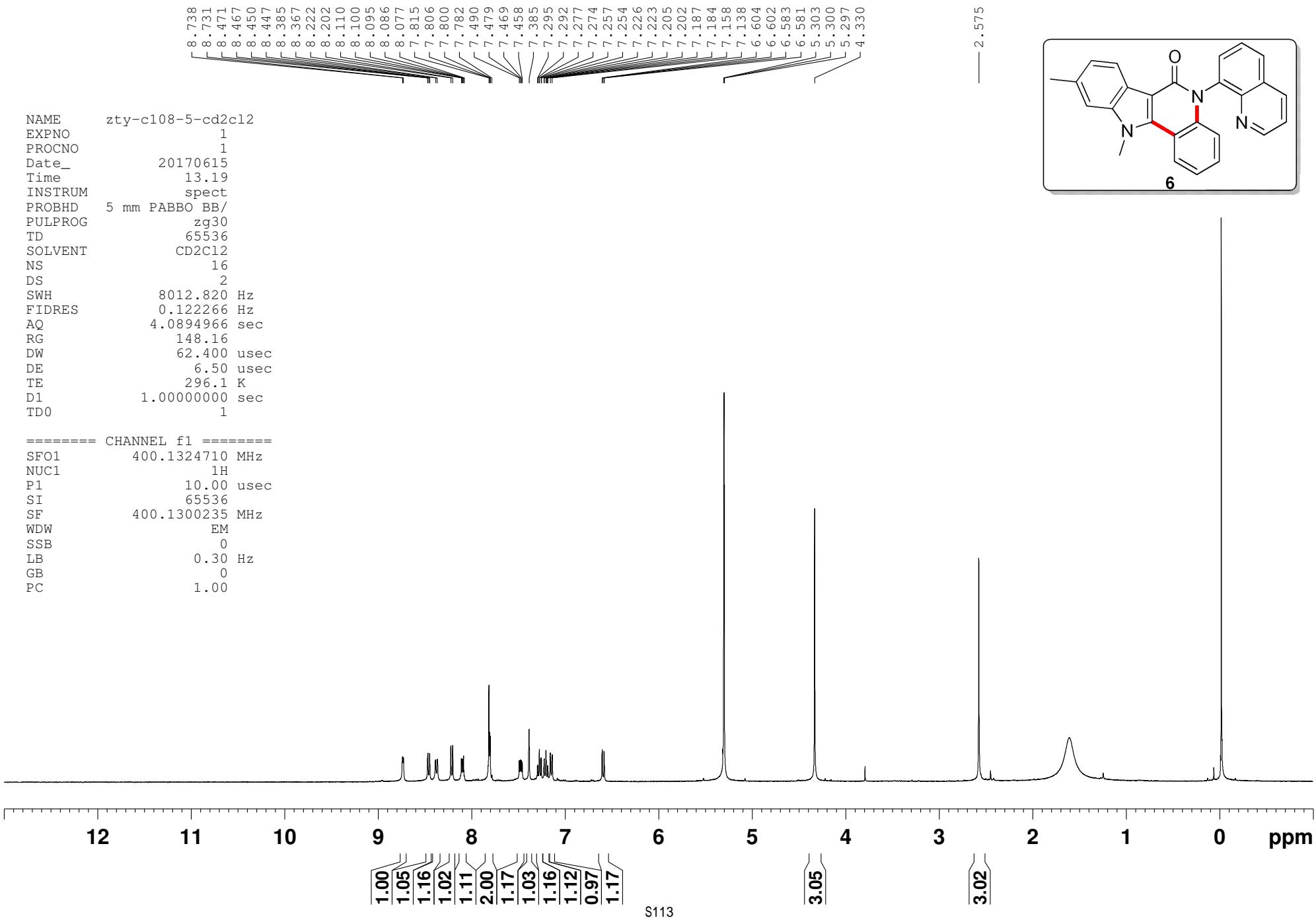




NAME zty-c108-6-cd2c12
 EXPNO 2
 PROCNO 1
 Date_ 20170615
 Time 15.22
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CD2C12
 NS 1000
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631988 sec
 RG 211.61
 DW 20.800 usec
 DE 6.50 usec
 TE 296.9 K
 D1 2.0000000 sec
 D11 0.0300000 sec
 TD0 1

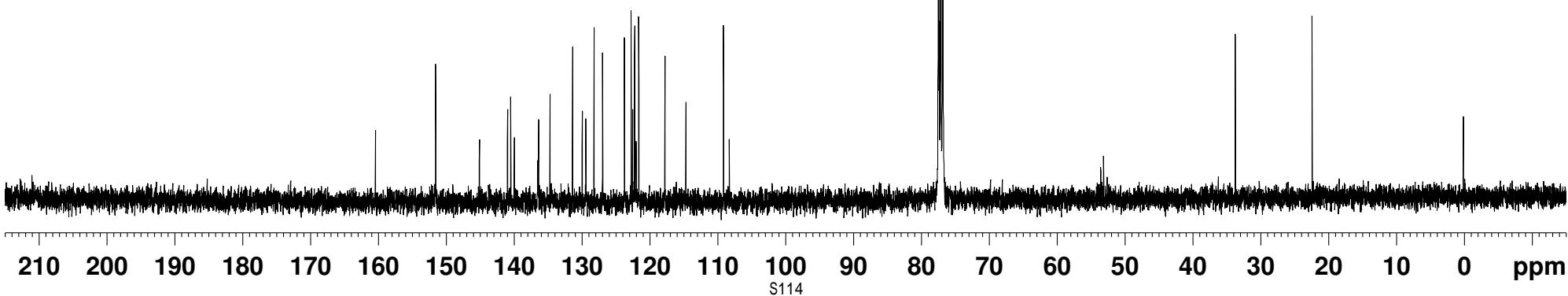
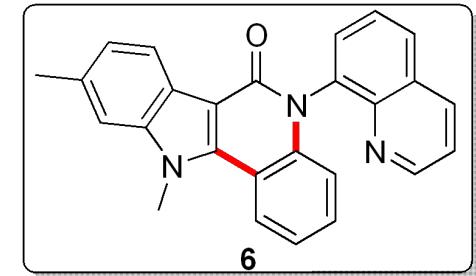
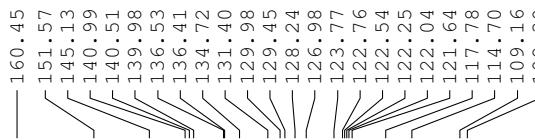
===== CHANNEL f1 =====
 SFO1 100.6228293 MHz
 NUC1 13C
 P1 10.00 usec
 SI 32768
 SF 100.6127298 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

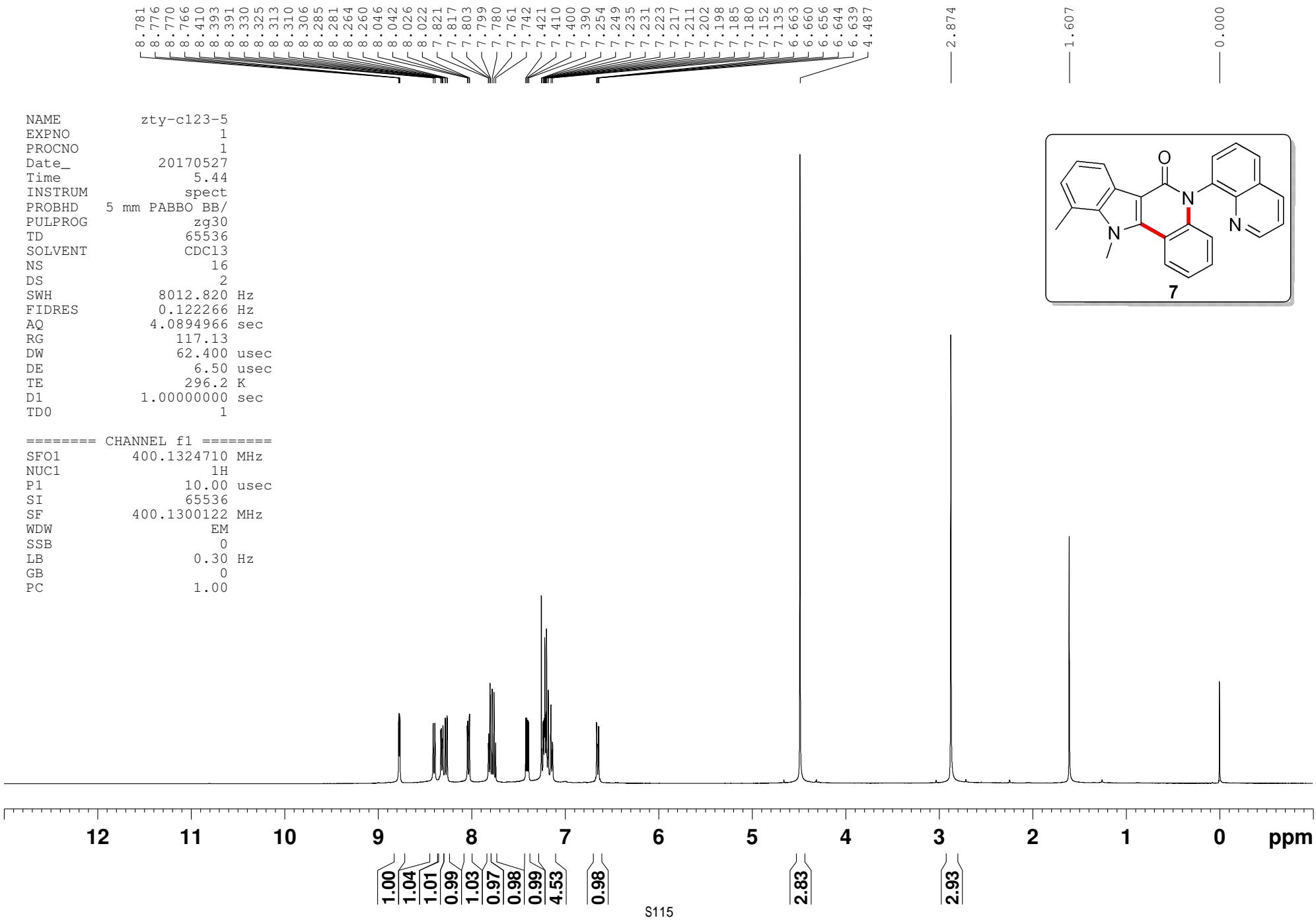




NAME zty-c108-5-cdc13
 EXPNO 2
 PROCNO 1
 Date_ 20170630
 Time 2.55
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 2000
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631988 sec
 RG 211.61
 DW 20.800 usec
 DE 6.50 usec
 TE 298.6 K
 D1 2.0000000 sec
 D11 0.0300000 sec
 TDO 1

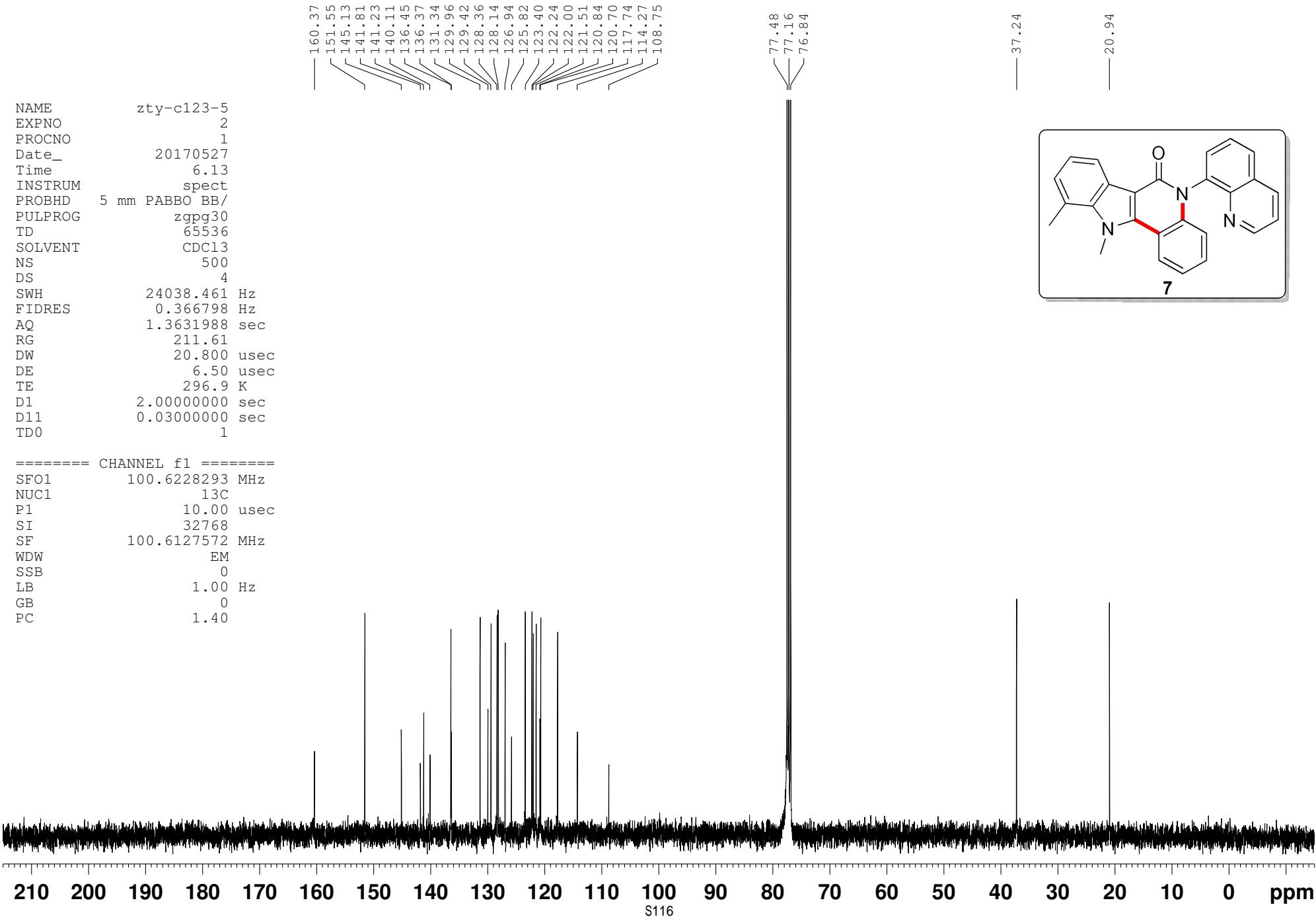
===== CHANNEL f1 =====
 SFO1 100.6228293 MHz
 NUC1 13C
 P1 10.00 usec
 SI 32768
 SF 100.6127552 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

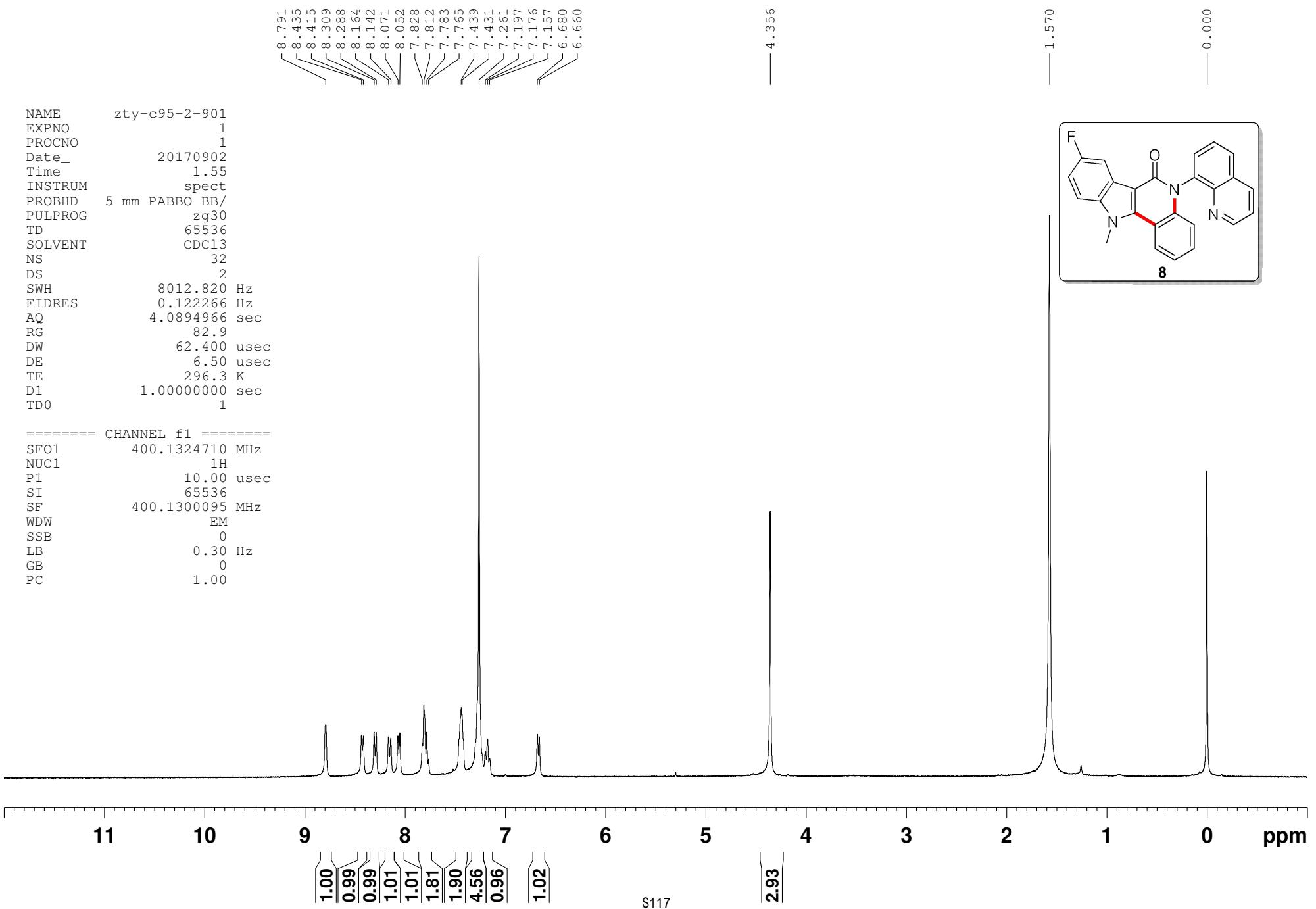


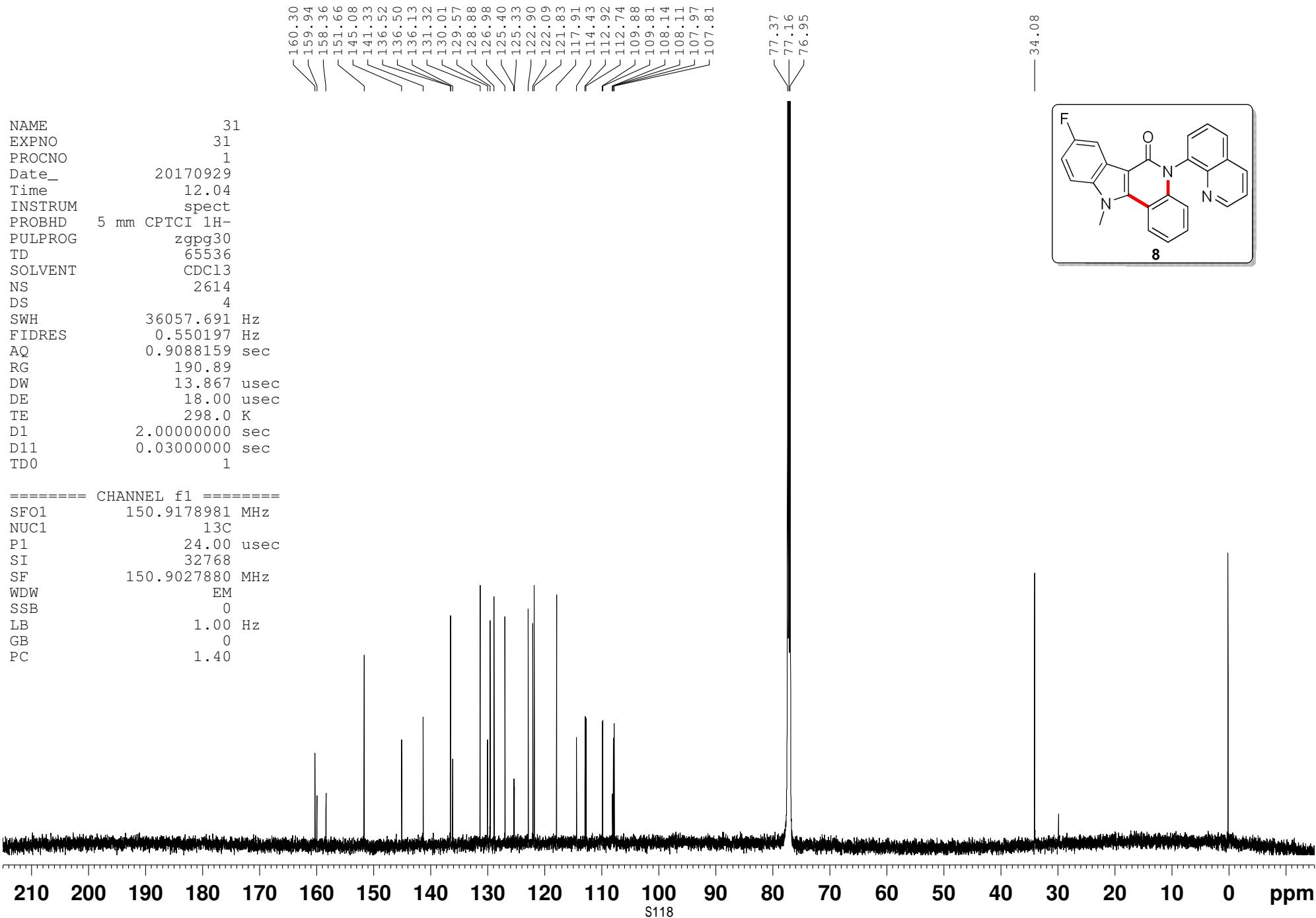


NAME zty-c123-5
 EXPNO 2
 PROCNO 1
 Date_ 20170527
 Time 6.13
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl₃
 NS 500
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631988 sec
 RG 211.61
 DW 20.800 usec
 DE 6.50 usec
 TE 296.9 K
 D1 2.0000000 sec
 D11 0.0300000 sec
 TDO 1

===== CHANNEL f1 ======
 SFO1 100.6228293 MHz
 NUC1 ¹³C
 P1 10.00 usec
 SI 32768
 SF 100.6127572 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40







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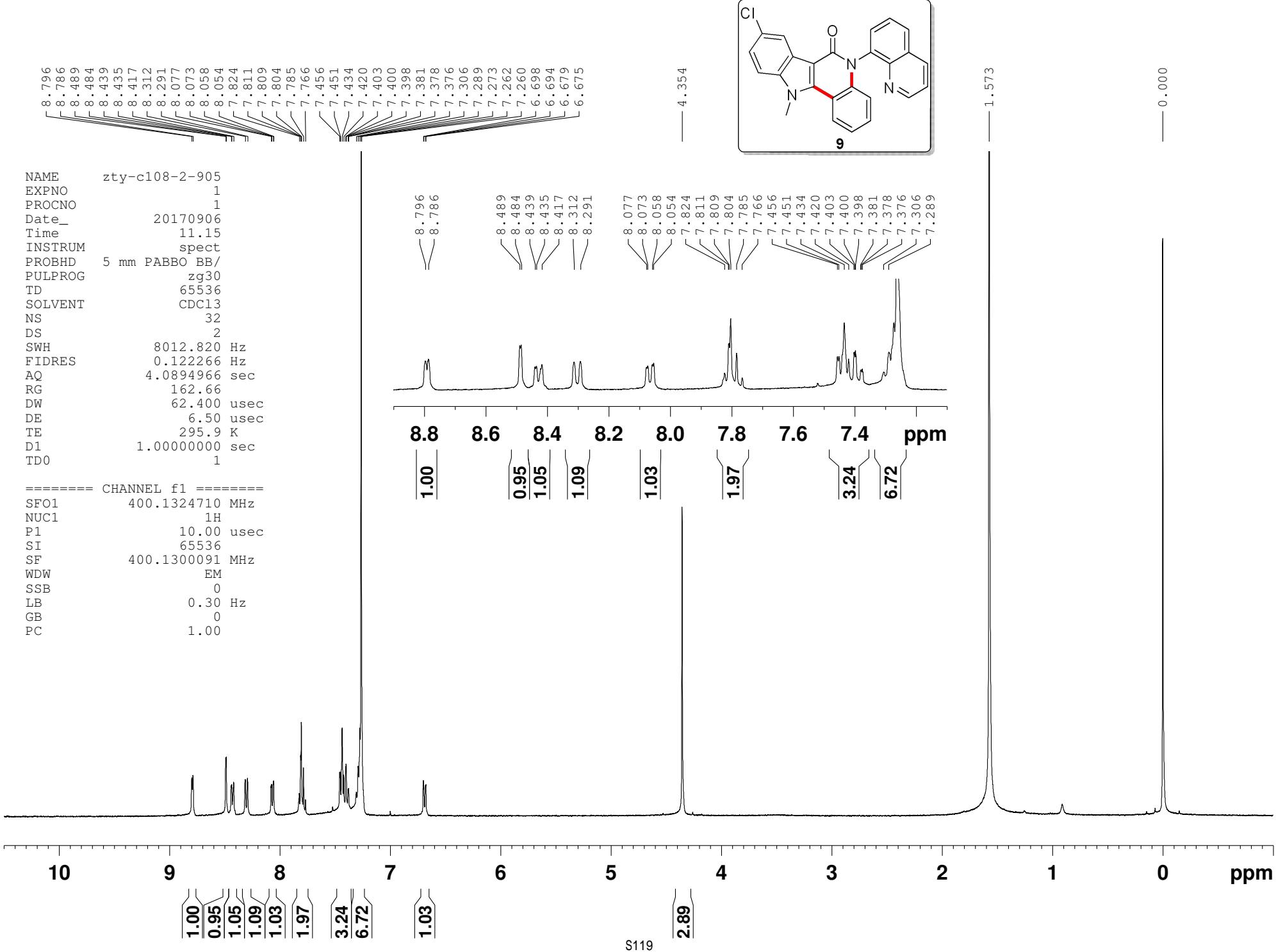
NAME      zty-c108-2-905
EXPNO          1
PROCNO         1
Date_        20170906
Time         11.15
INSTRUM      spect
PROBHD      5 mm PABBO BB/
PULPROG      zg30
TD            65536
SOLVENT      CDC13
NS             32
DS              2
SWH           8012.820 Hz
FIDRES      0.122266 Hz
AQ            4.0894966 sec
RG            162.66
DW            62.400 usec
DE             6.50 usec
TE             295.9 K
D1       1.00000000 sec
TDO            1

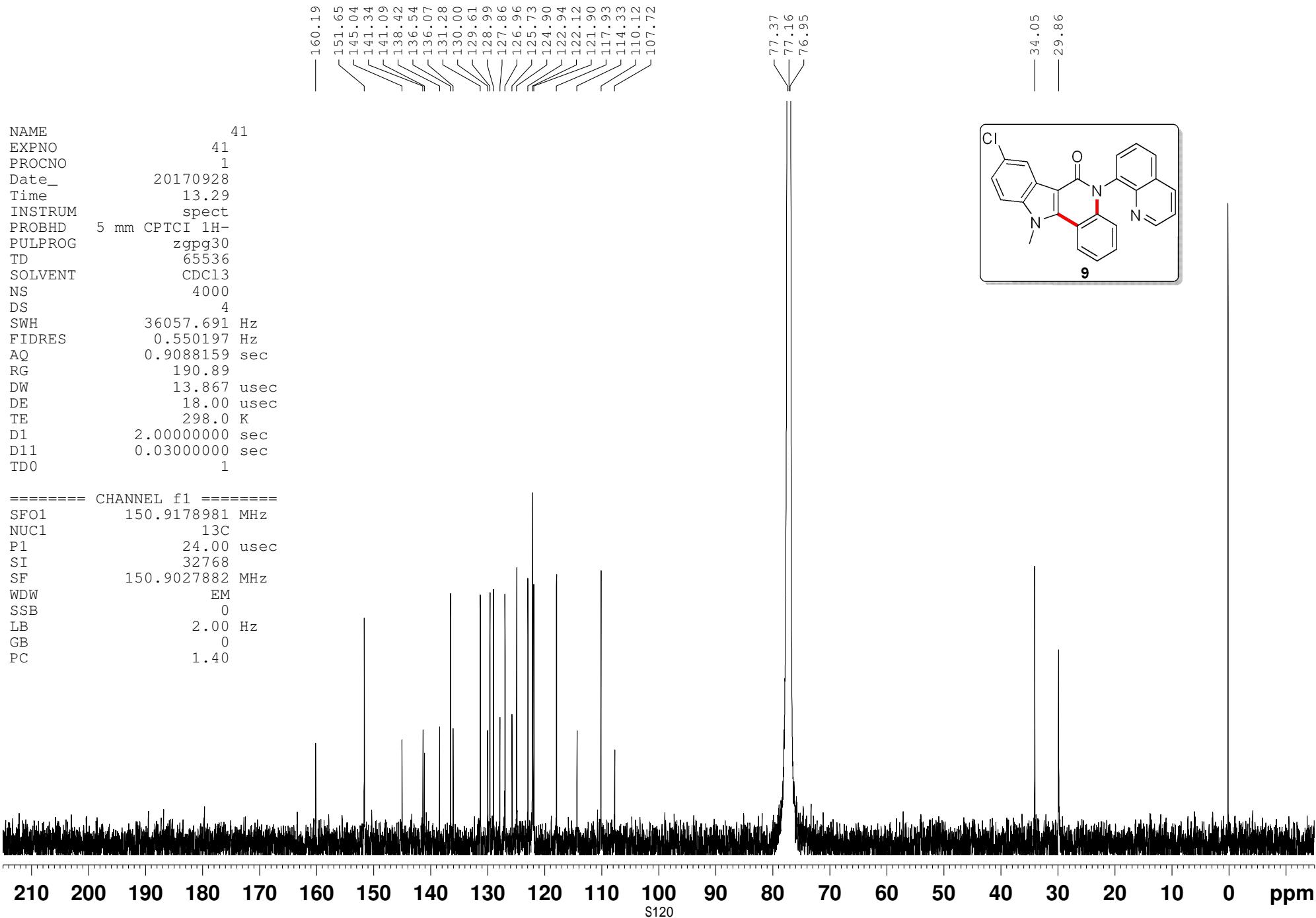
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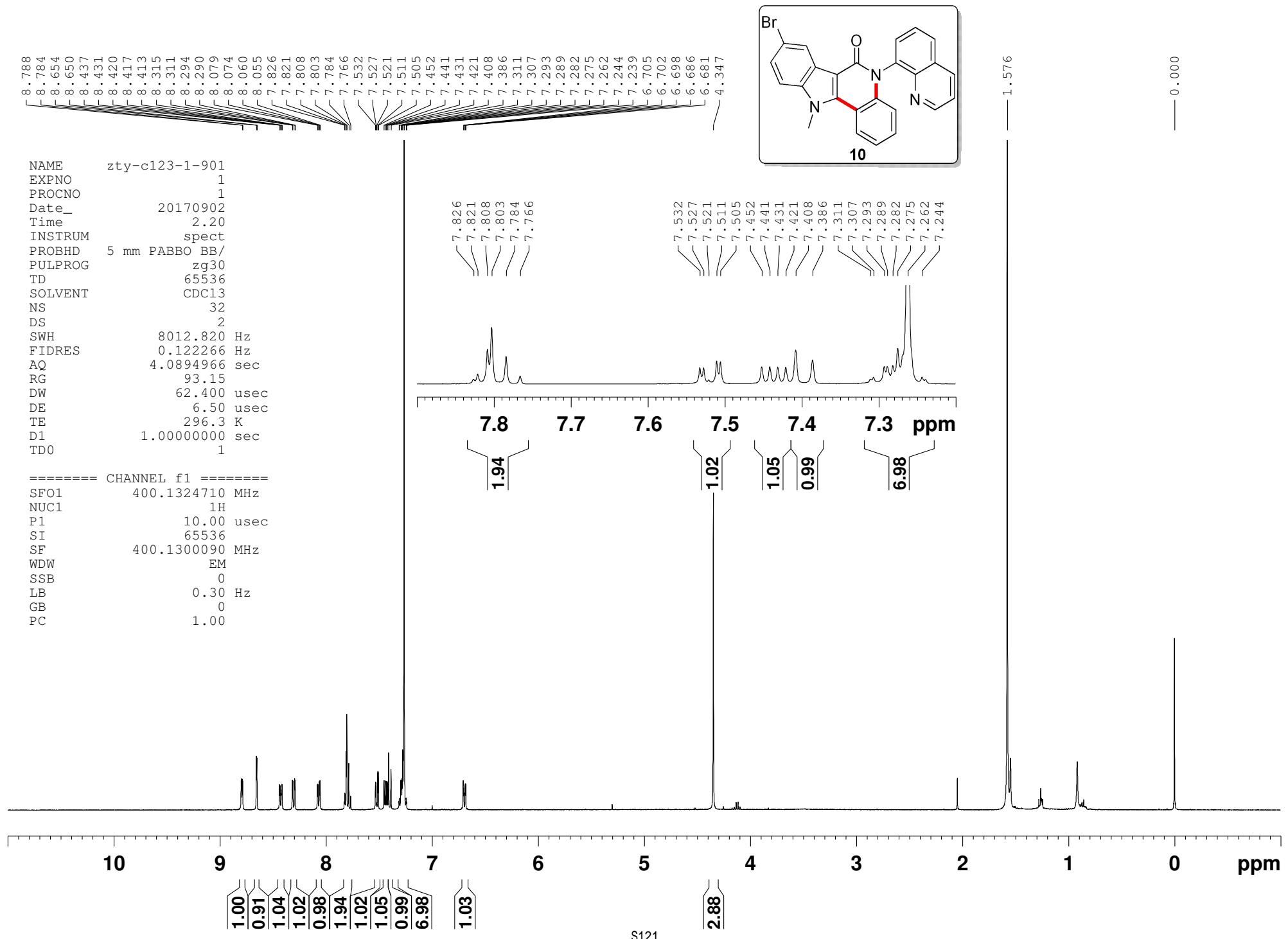
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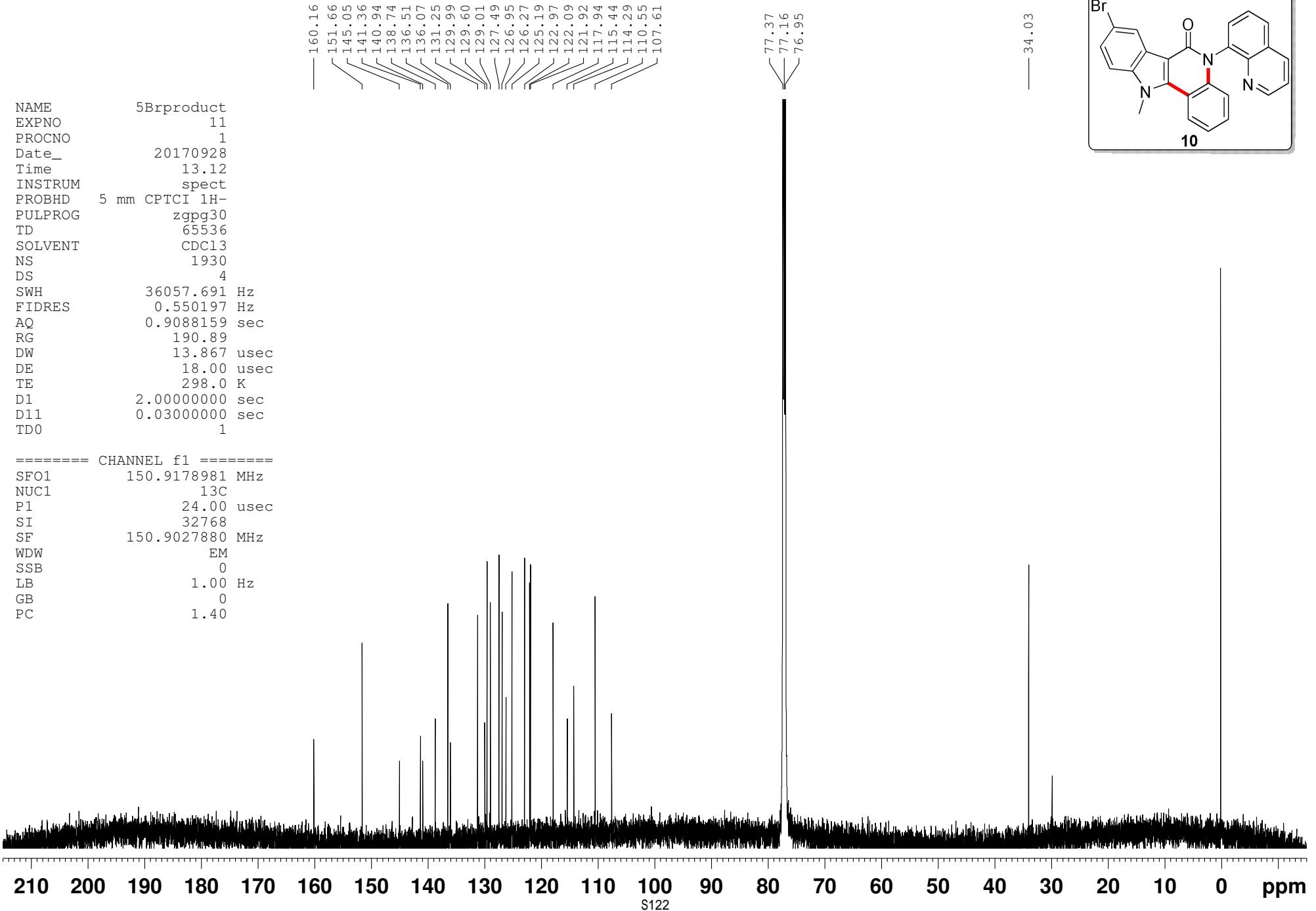
===== CHANNEL f1 =====
SFO1          400.1324710 MHz
NUC1           1H
P1              10.00 usec
SI              65536
SF          400.1300091 MHz
WDW             EM
SSB              0
LB              0.30 Hz
GB              0
PC              1.00

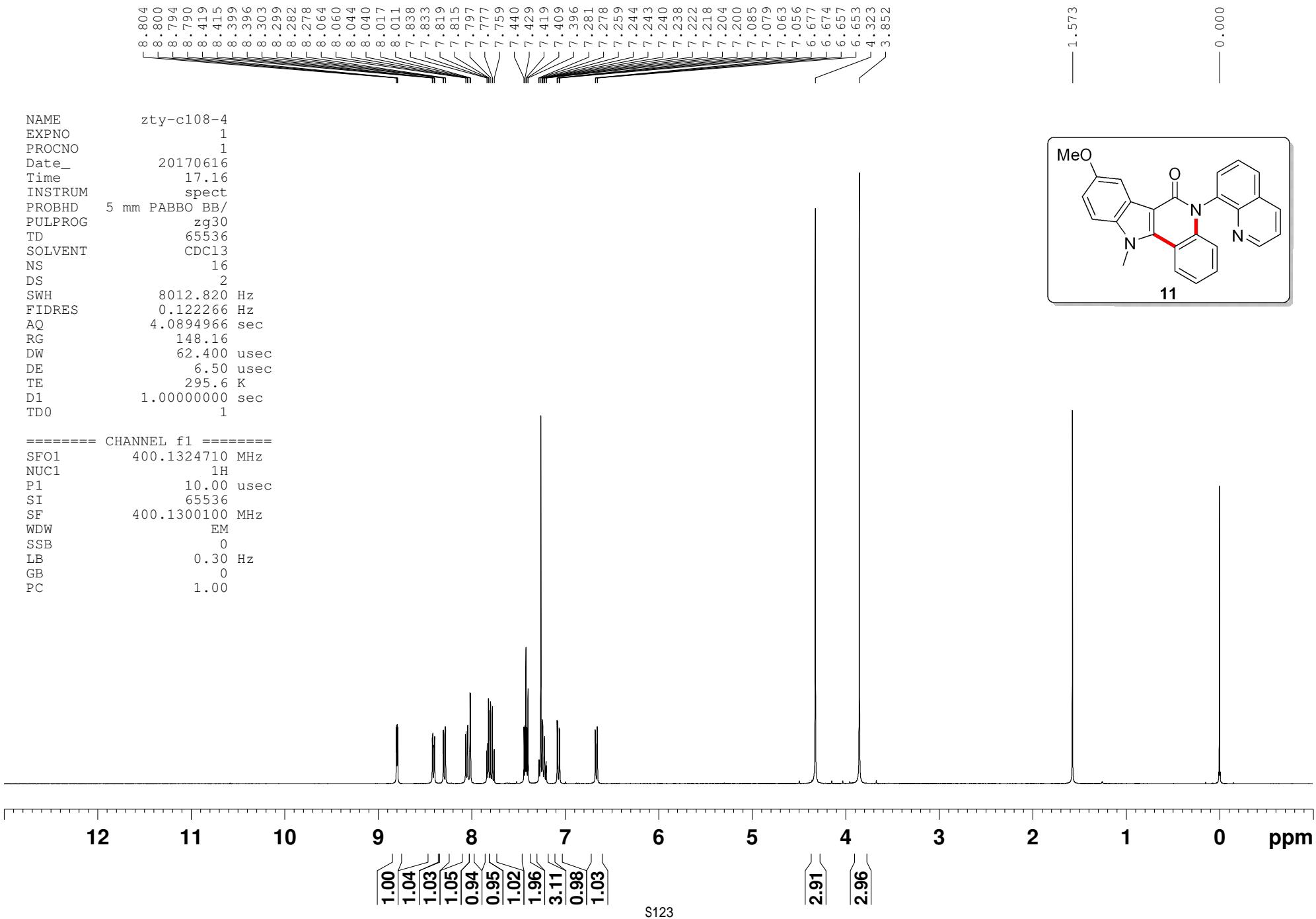
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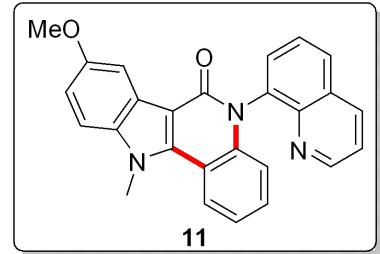
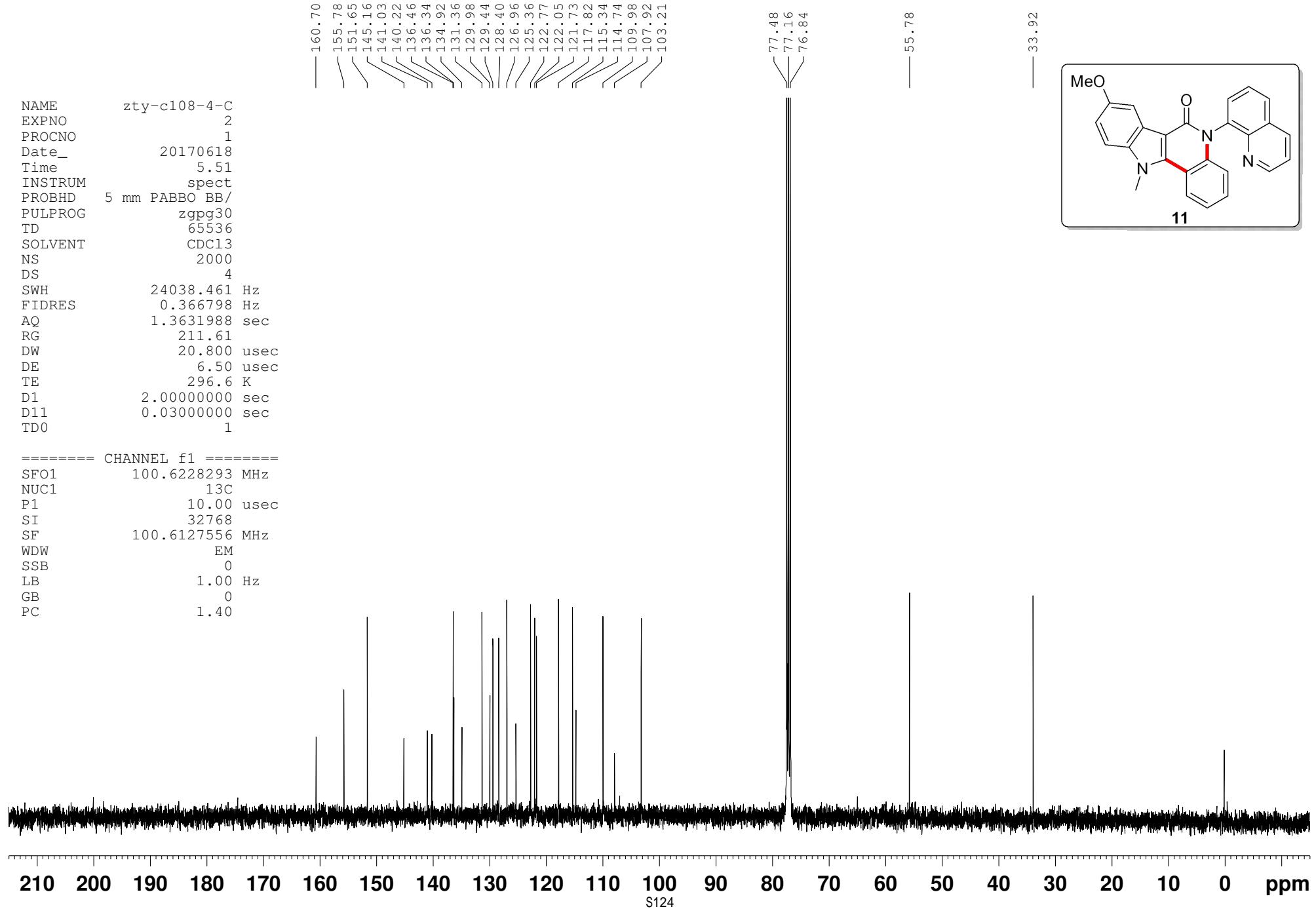
NAME          zty-c108-4-C
EXPNO         2
PROCNO        1
Date_         20170618
Time          5.51
INSTRUM       spect
PROBHD        5 mm PABBO BB/
PULPROG      zgpg30
TD            65536
SOLVENT       CDC13
NS            2000
DS             4
SWH           24038.461 Hz
FIDRES        0.366798 Hz
AQ            1.3631988 sec
RG            211.61
DW            20.800 usec
DE            6.50  usec
TE            296.6 K
D1           2.000000000 sec
D11          0.030000000 sec
TDO           1

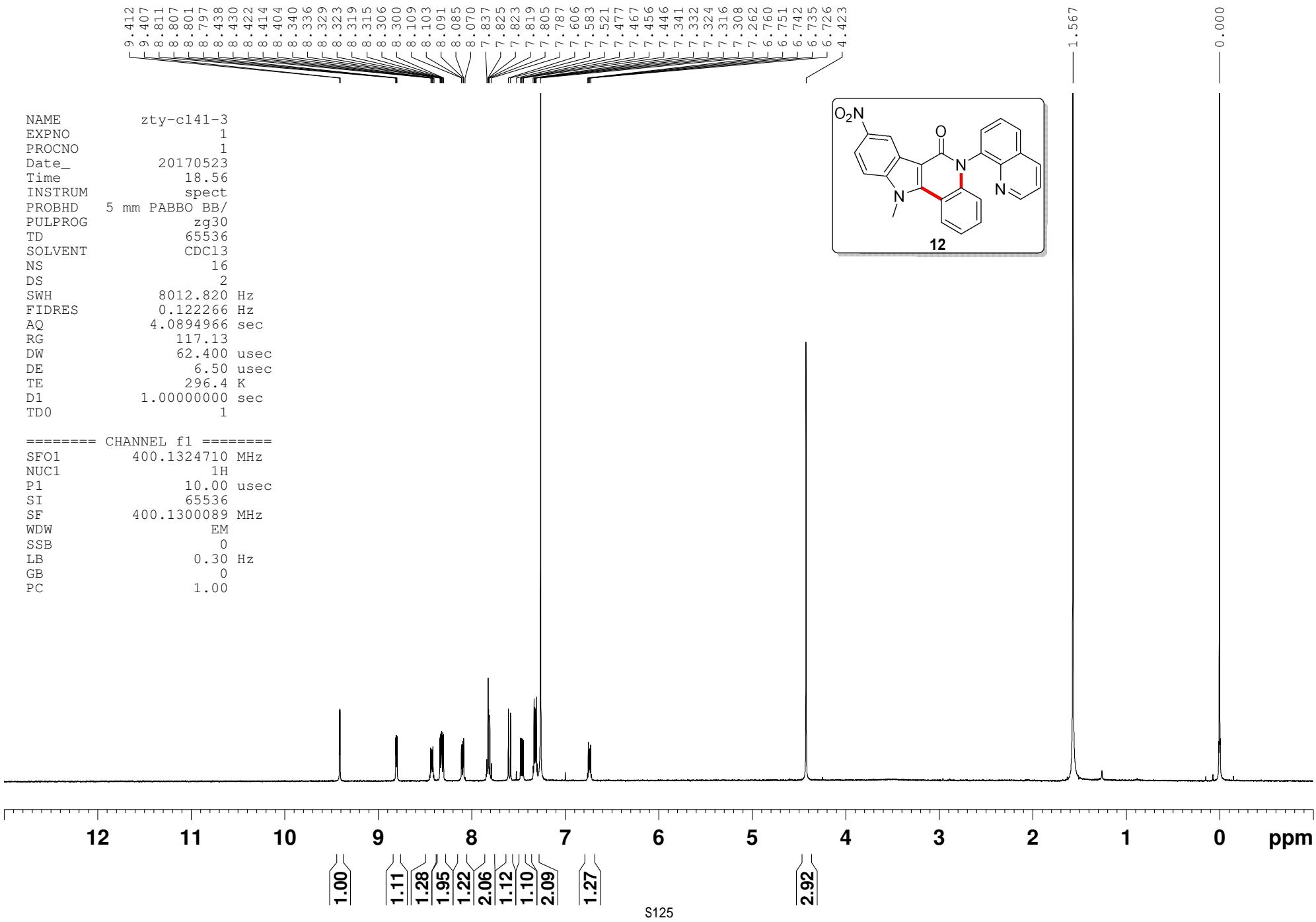
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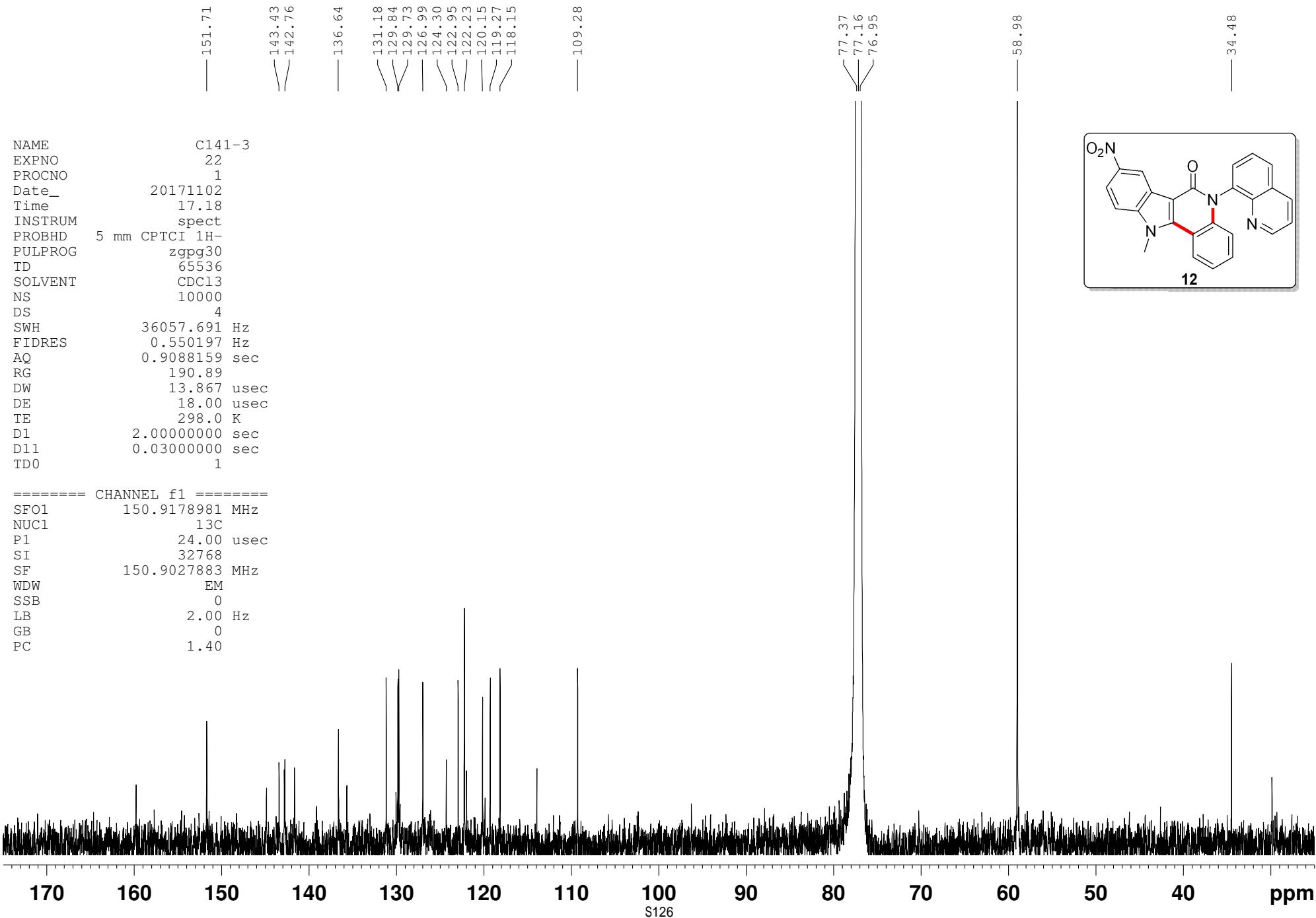
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===== CHANNEL f1 =====
SFO1          100.6228293 MHz
NUC1           13C
P1             10.00 usec
SI              32768
SF          100.6127556 MHz
WDW            EM
SSB             0
LB             1.00 Hz
GB             0
PC             1.40

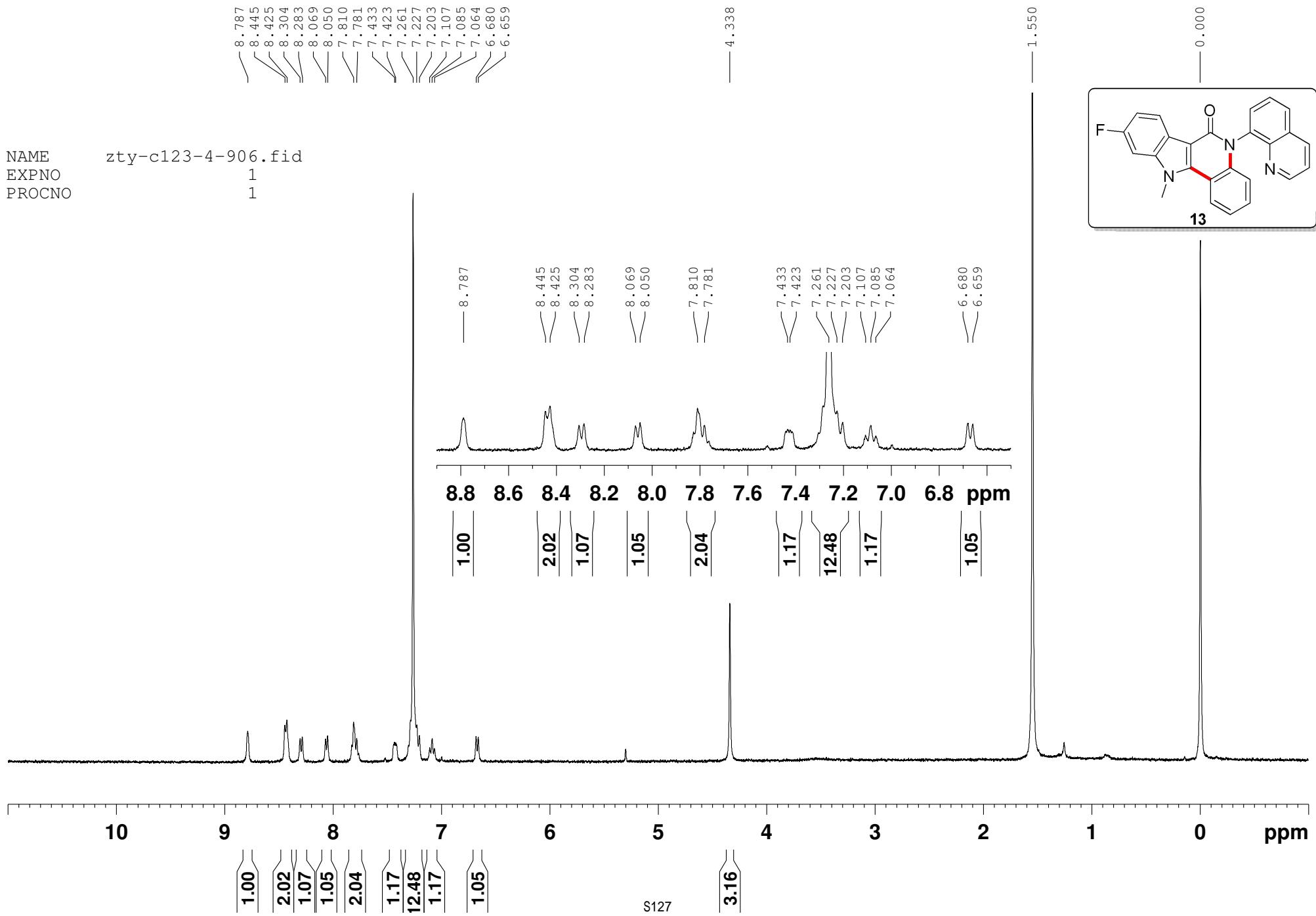
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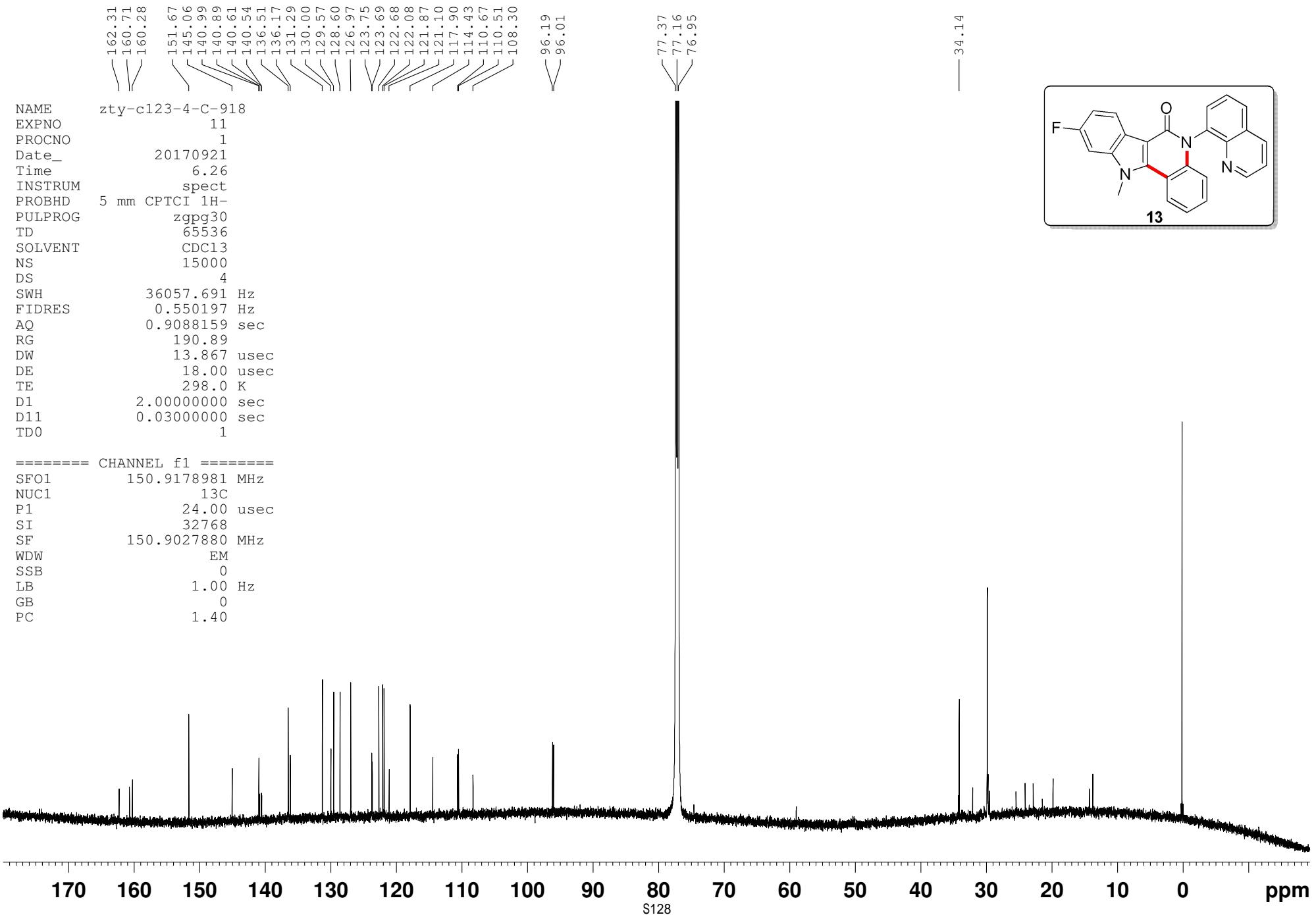


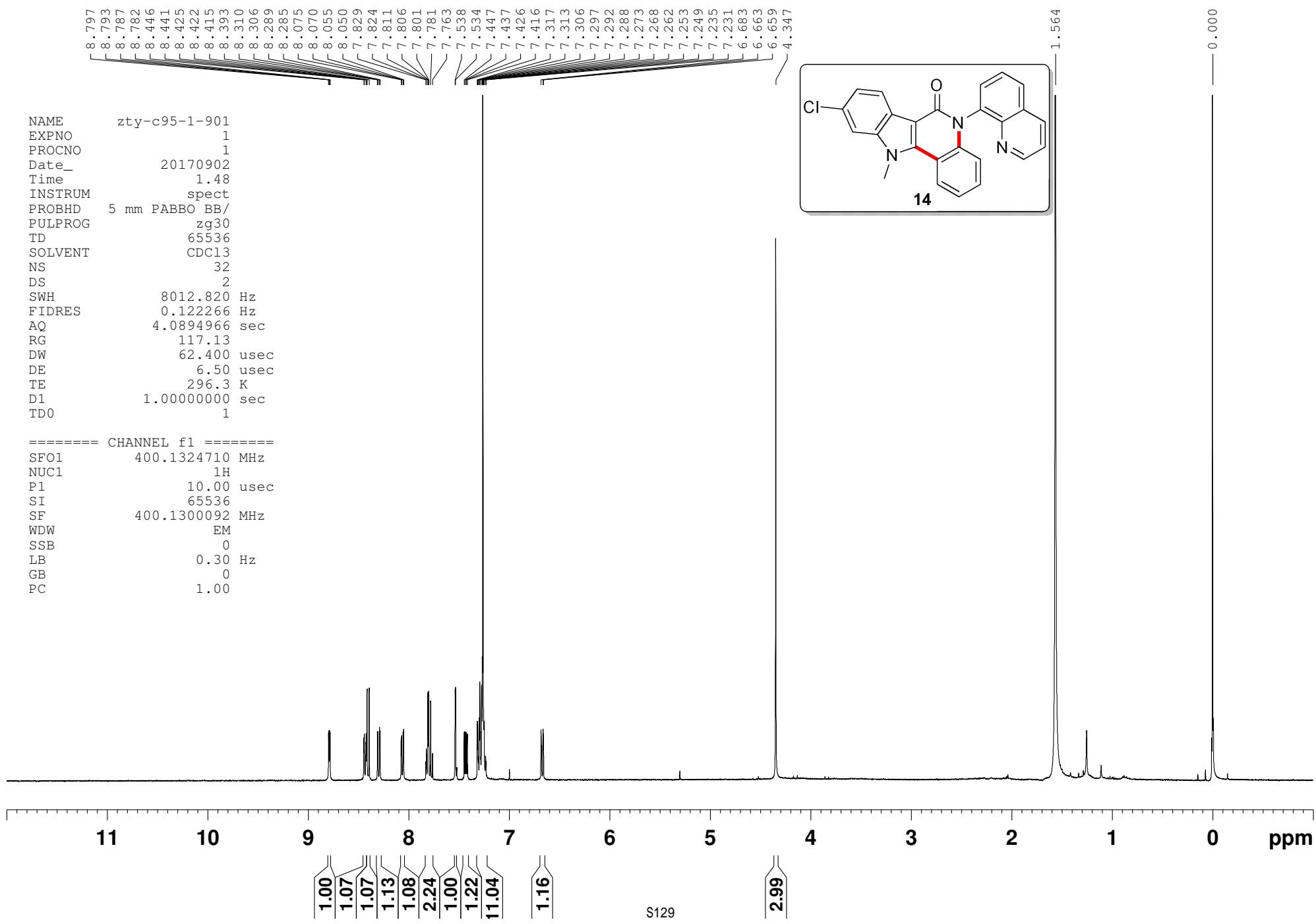




NAME zty-c123-4-906.fid
EXPNO 1
PROCNO 1

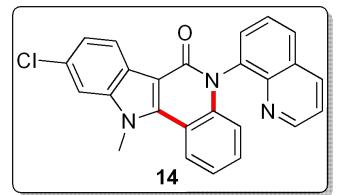
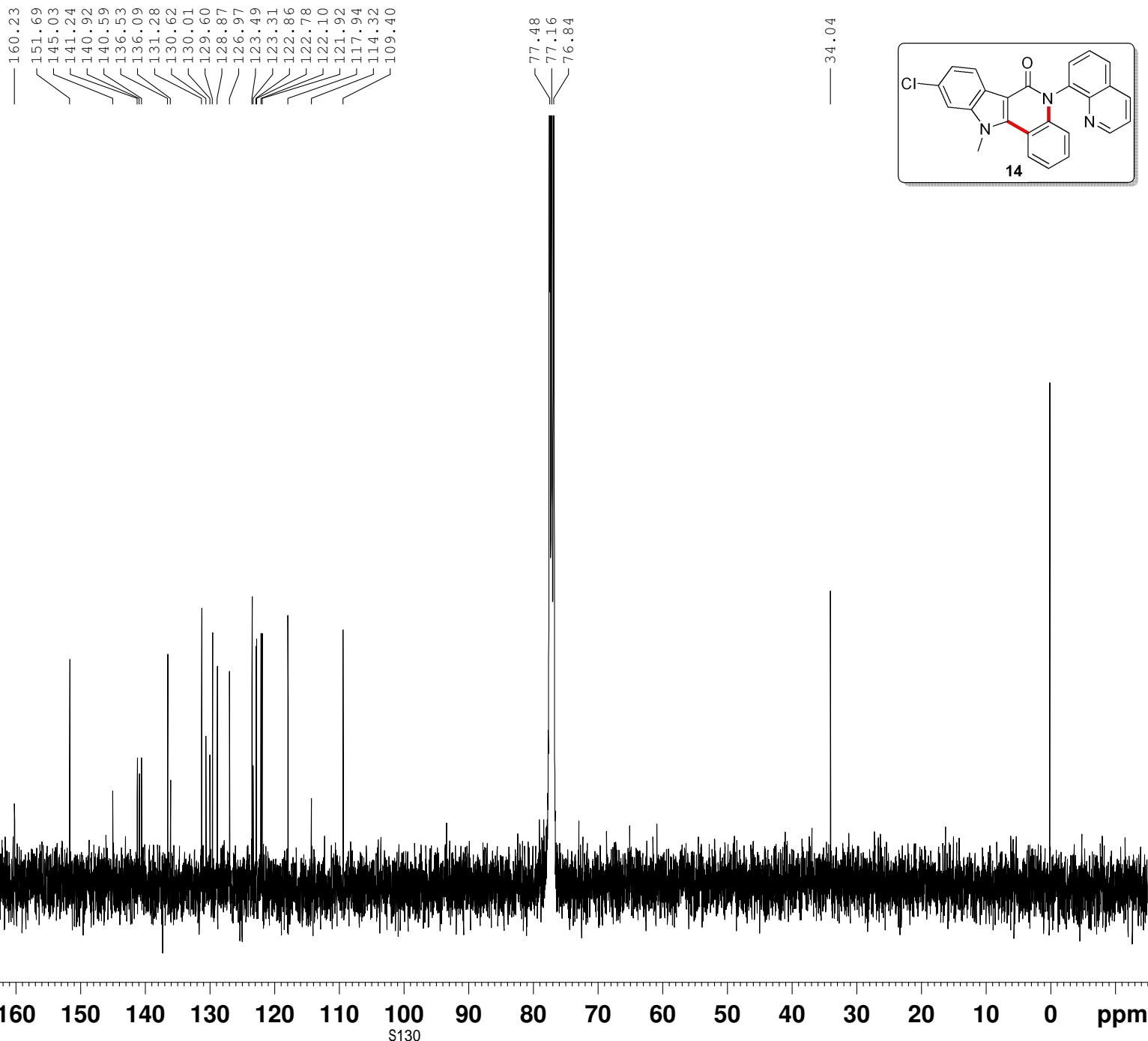


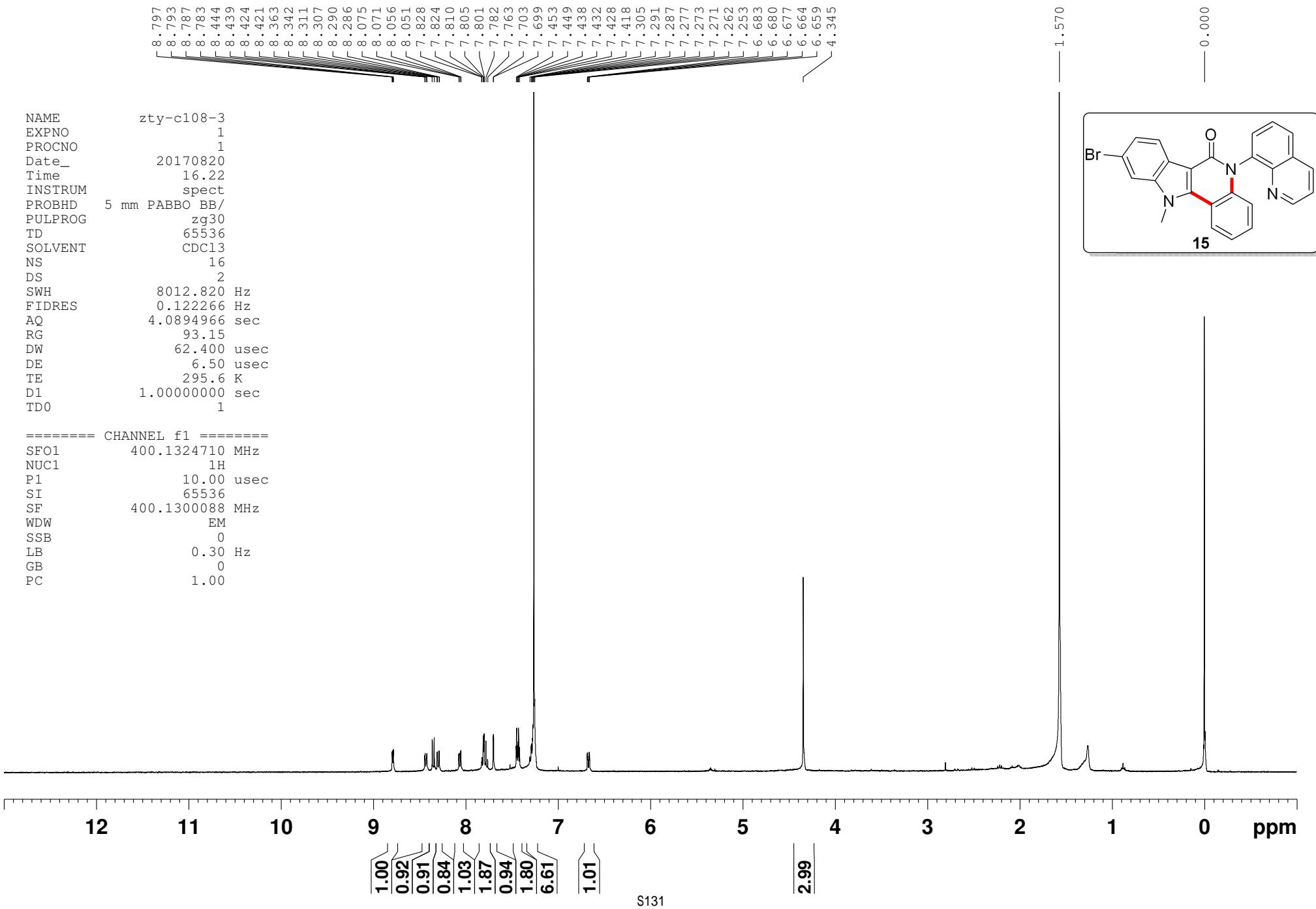




NAME ZTY-C95-1-901-8h
 EXPNO 1
 PROCNO 1
 Date_ 20170915
 Time 11.53
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl₃
 NS 8000
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631988 sec
 RG 211.61
 DW 20.800 usec
 DE 6.50 usec
 TE 296.0 K
 D1 2.0000000 sec
 D11 0.03000000 sec
 TD0 1

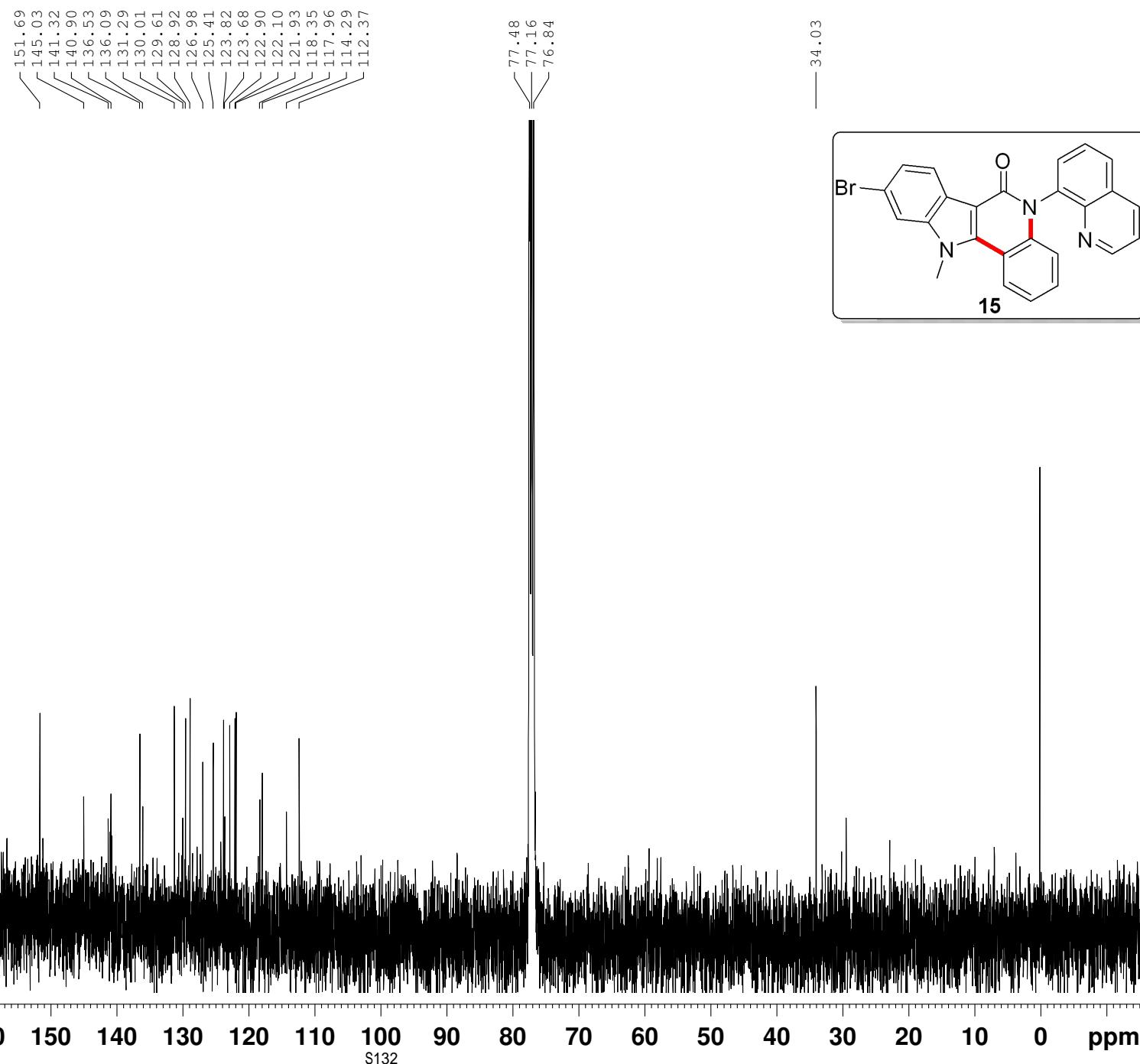
===== CHANNEL f1 ======
 SFO1 100.6228293 MHz
 NUC1 13C
 P1 10.00 usec
 SI 32768
 SF 100.6127551 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

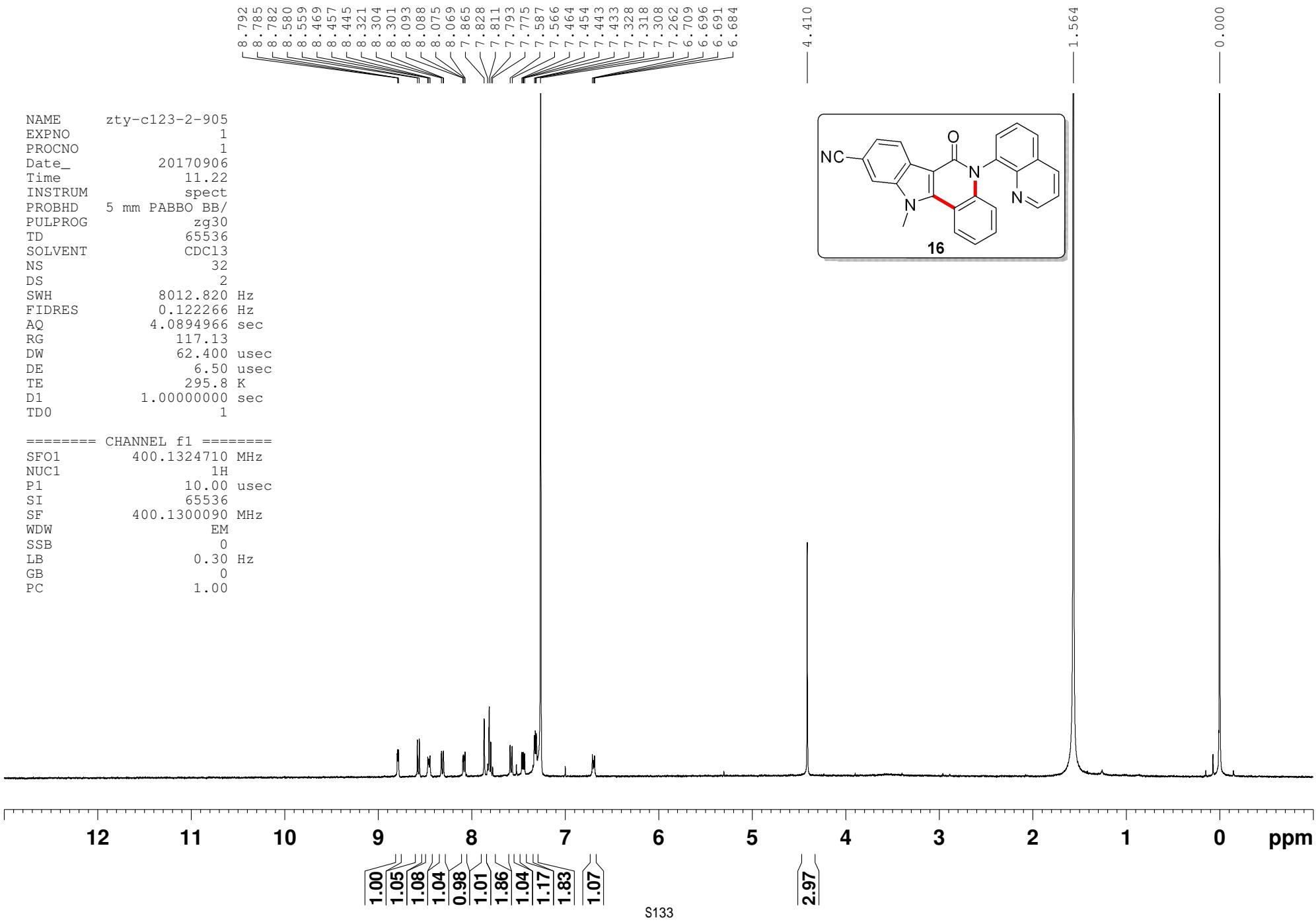


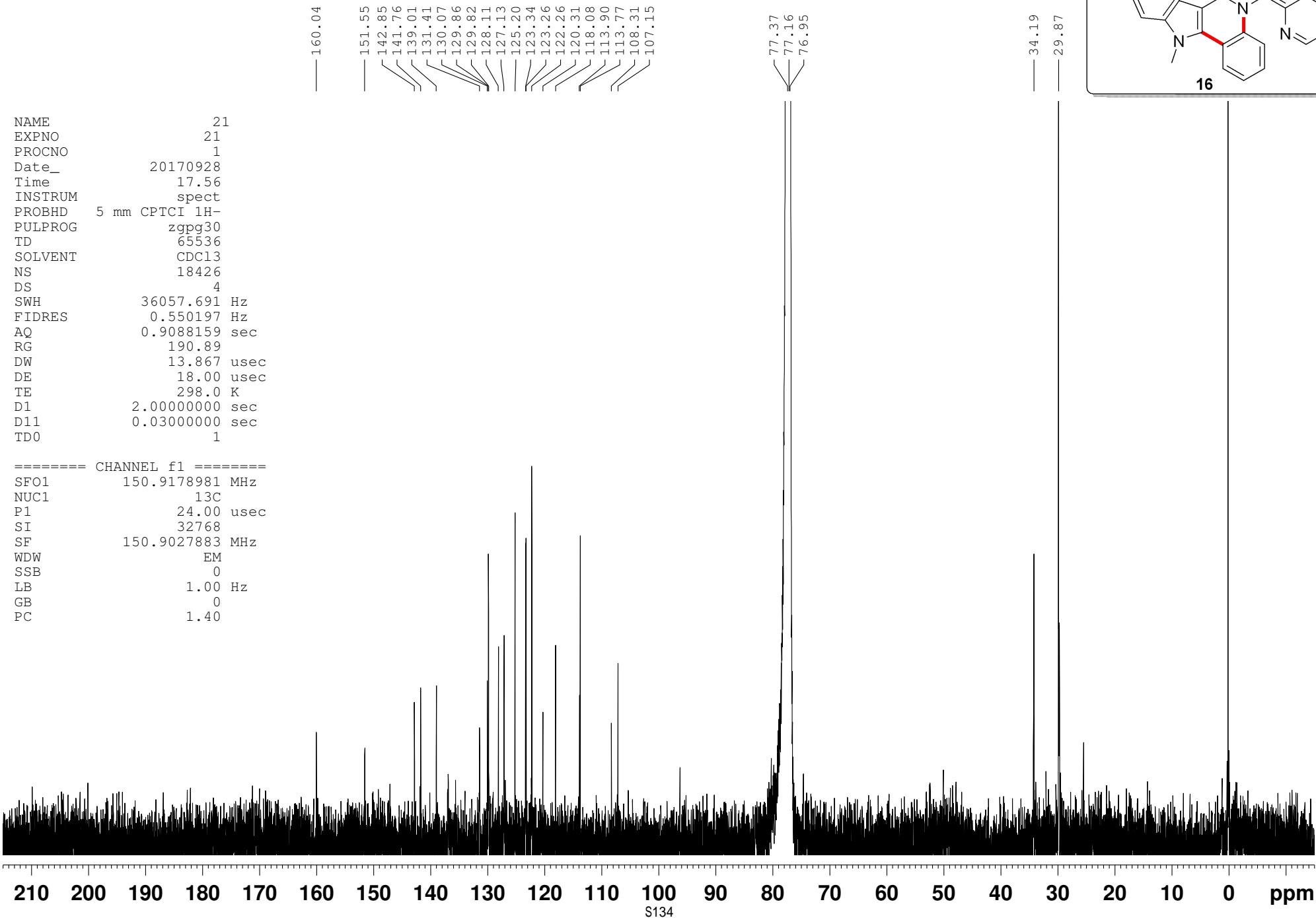


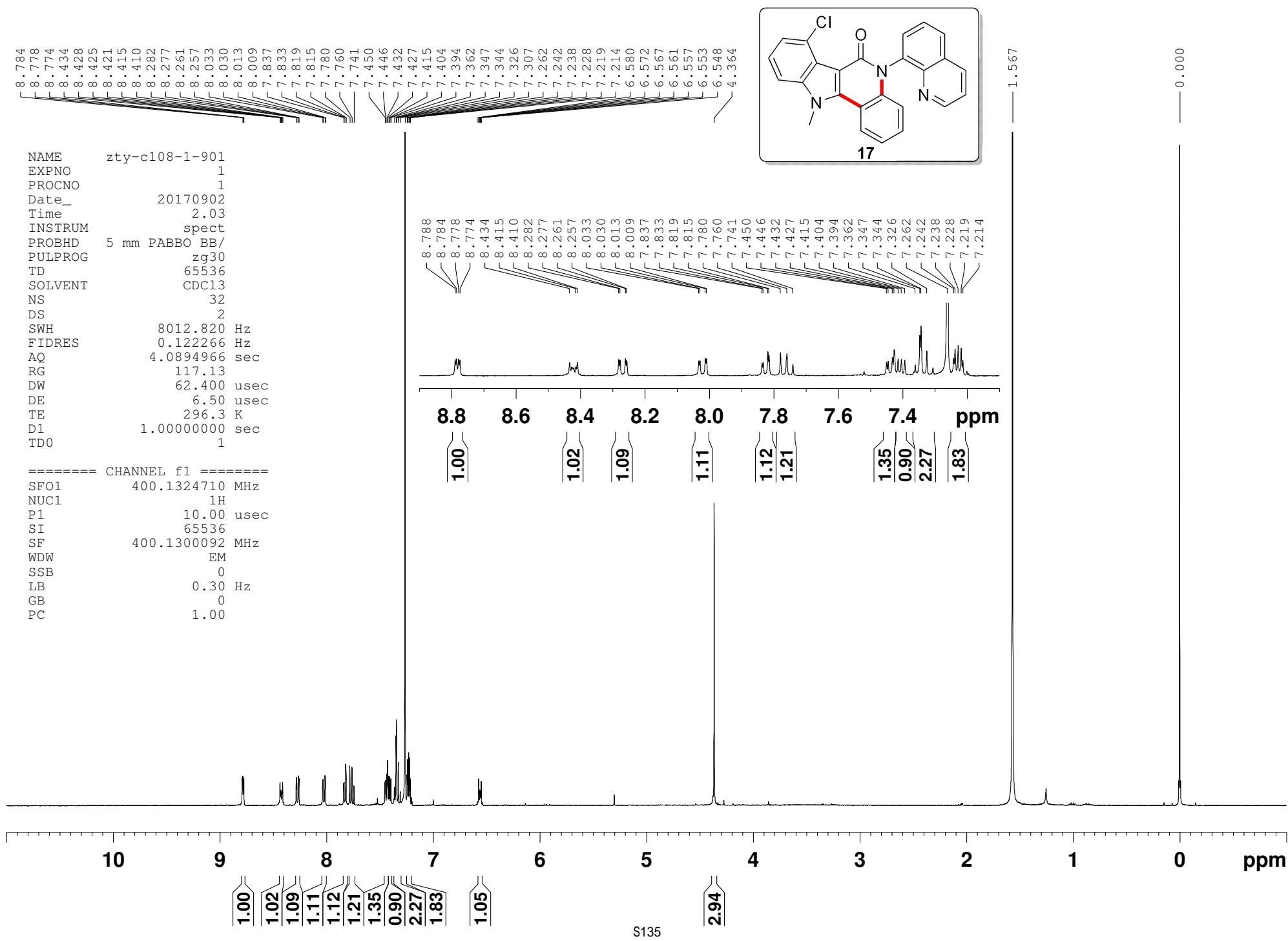
NAME zty-c108-3-c
 EXPNO 1
 PROCNO 1
 Date_ 20170823
 Time 0.34
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 4000
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631988 sec
 RG 211.61
 DW 20.800 usec
 DE 6.50 usec
 TE 298.0 K
 D1 2.0000000 sec
 D11 0.0300000 sec
 TDO 1

===== CHANNEL f1 =====
 SFO1 100.6228293 MHz
 NUC1 13C
 P1 10.00 usec
 SI 32768
 SF 100.6127543 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40









```

NAME      zty-c108-1-901
EXPNO          1
PROCNO        1
Date_    20170902
Time      2.03
INSTRUM   spect
PROBHD   5 mm PABBO BB/
PULPROG   zg30
TD        65536
SOLVENT    CDC13
NS           32
DS            2
SWH       8012.820 Hz
FIDRES   0.122266 Hz
AQ        4.0894966 sec
RG        117.13
DW        62.400 usec
DE         6.50 usec
TE        296.3 K
D1   1.000000000 sec
TDO          1

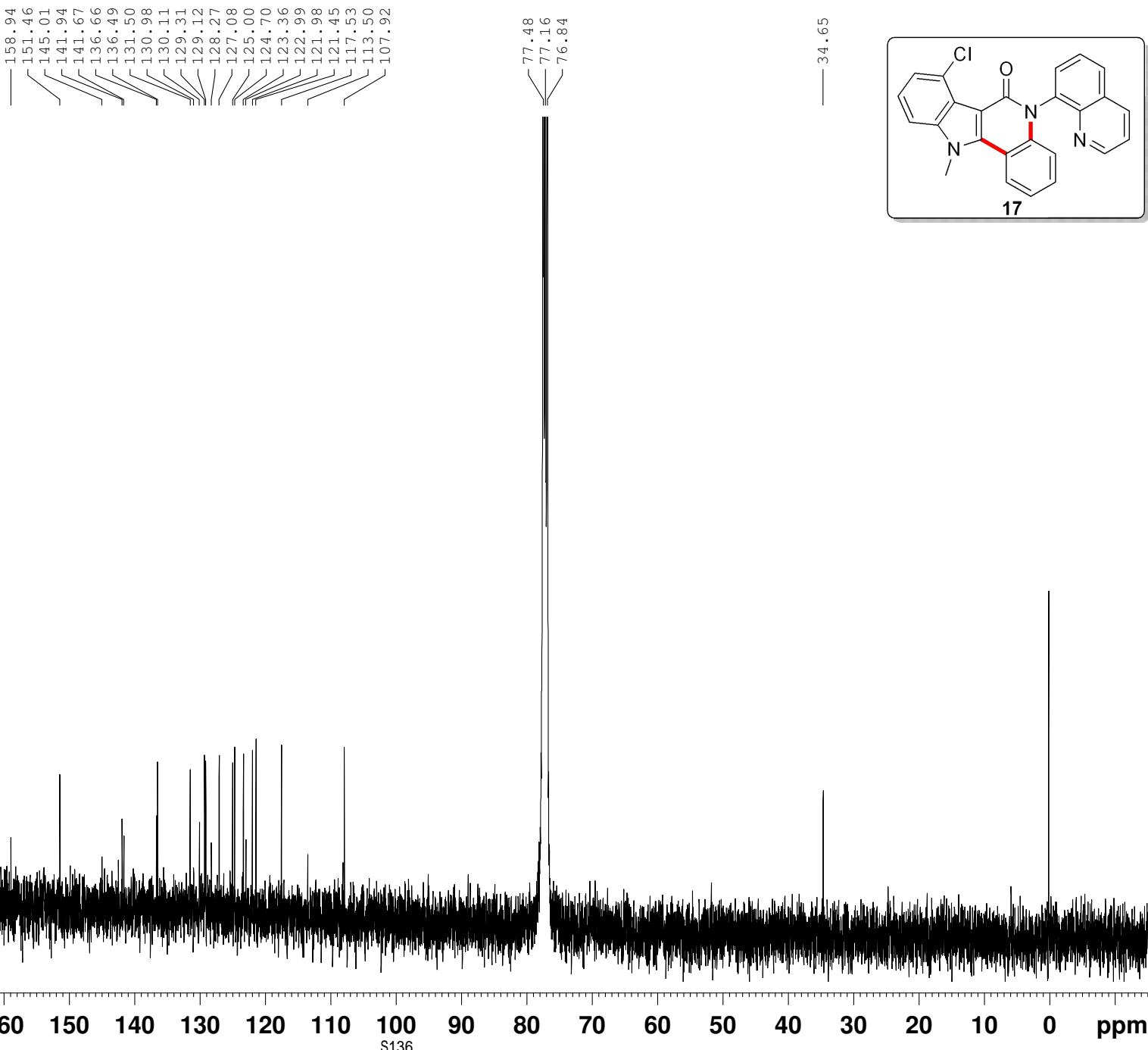
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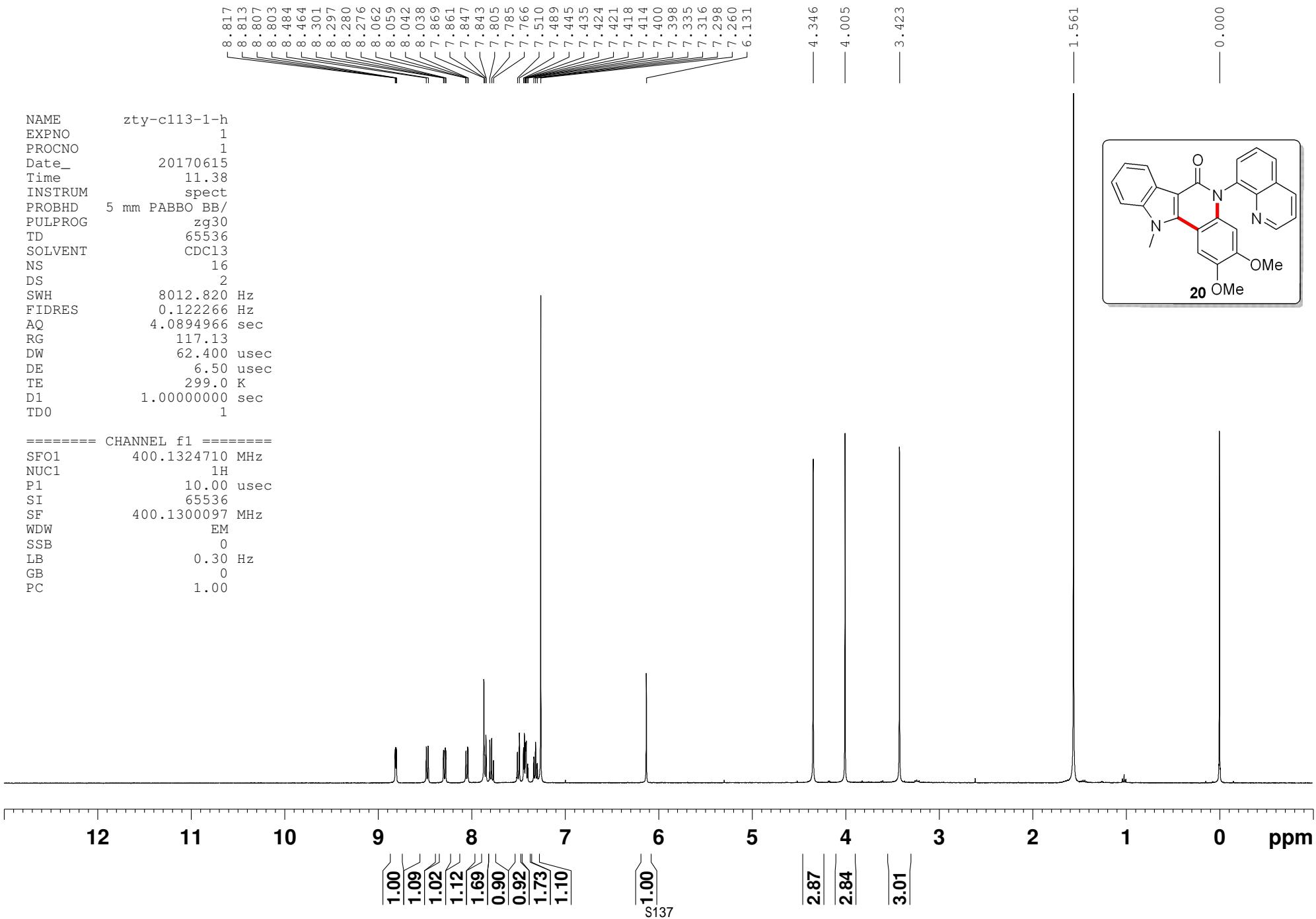
```
===== CHANNEL f1 =====
SFO1          400.1324710 MHz
NUC1           1H
P1             10.00 usec
SI              65536
SF          400.1300092 MHz
WDW            EM
SSB              0
LB             0.30 Hz
GB              0
PC             1.00
```

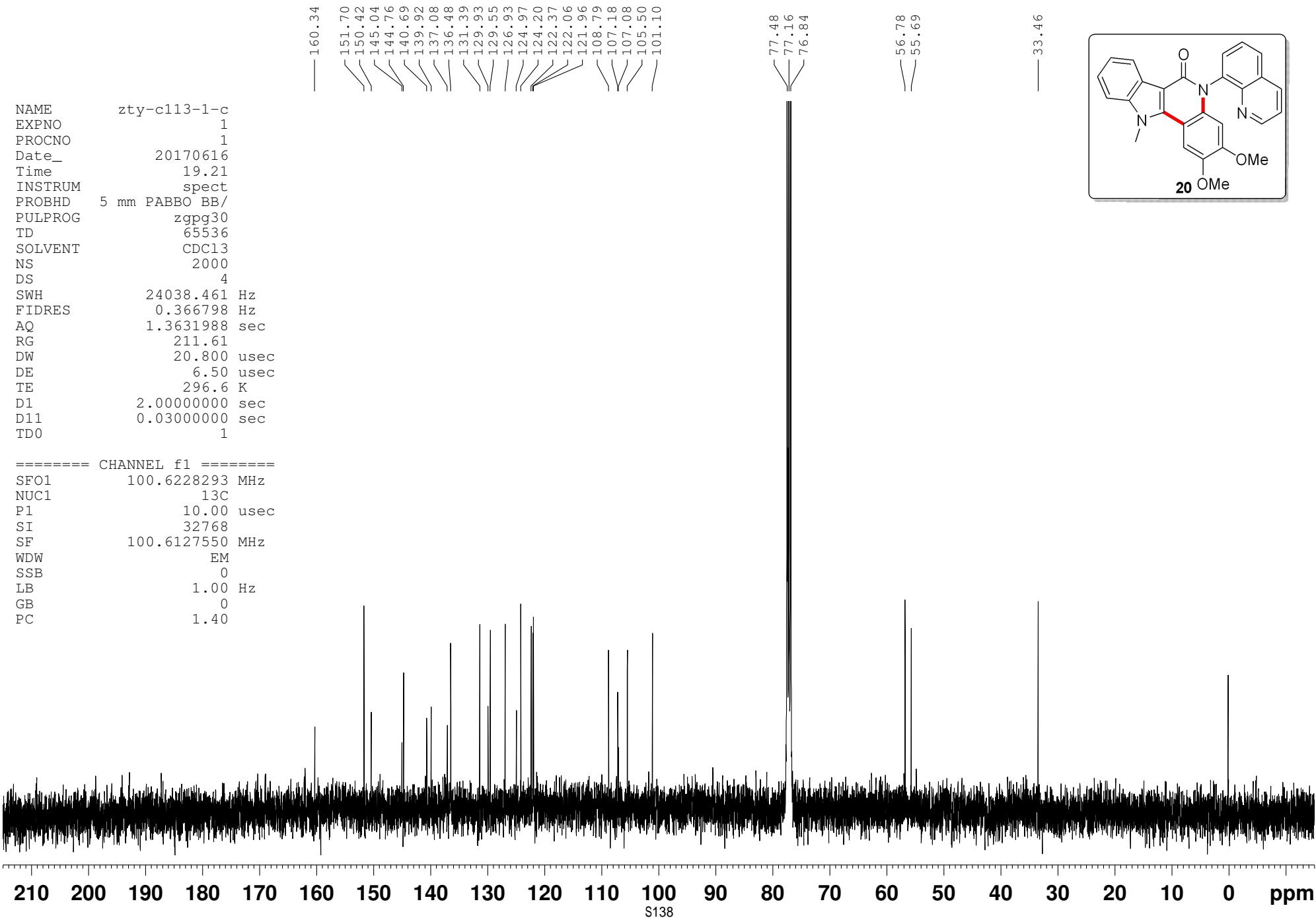
S135

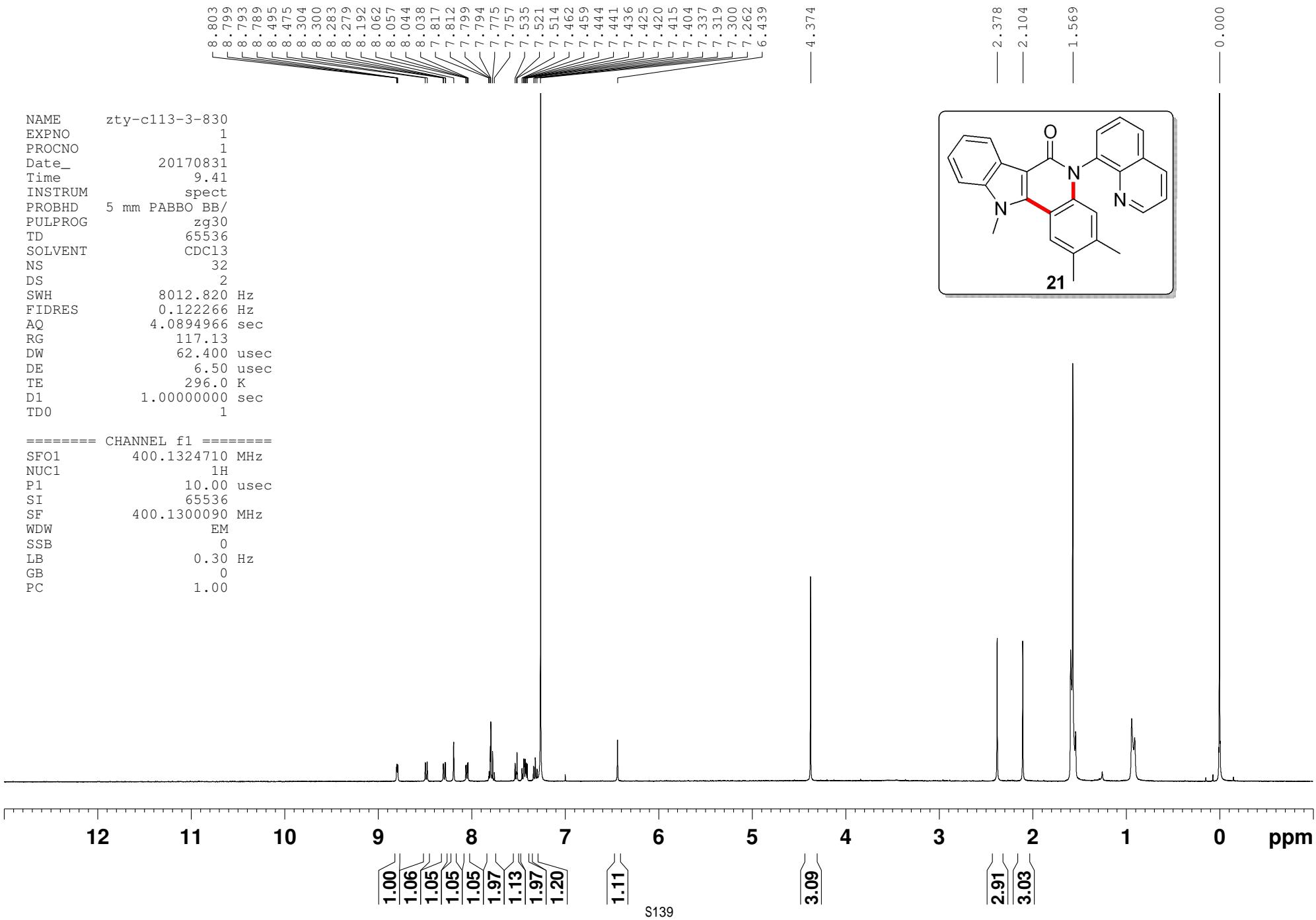
NAME zty-c108-1-901-8h
 EXPNO 1
 PROCNO 1
 Date_ 20170917
 Time 9.33
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl₃
 NS 8000
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631988 sec
 RG 211.61
 DW 20.800 usec
 DE 6.50 usec
 TE 296.2 K
 D1 2.0000000 sec
 D11 0.0300000 sec
 TDO 1

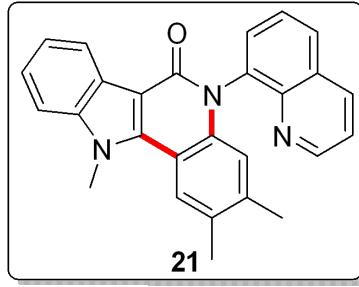
===== CHANNEL f1 ======
 SFO1 100.6228293 MHz
 NUC1 ¹³C
 P1 10.00 usec
 SI 32768
 SF 100.6127550 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40





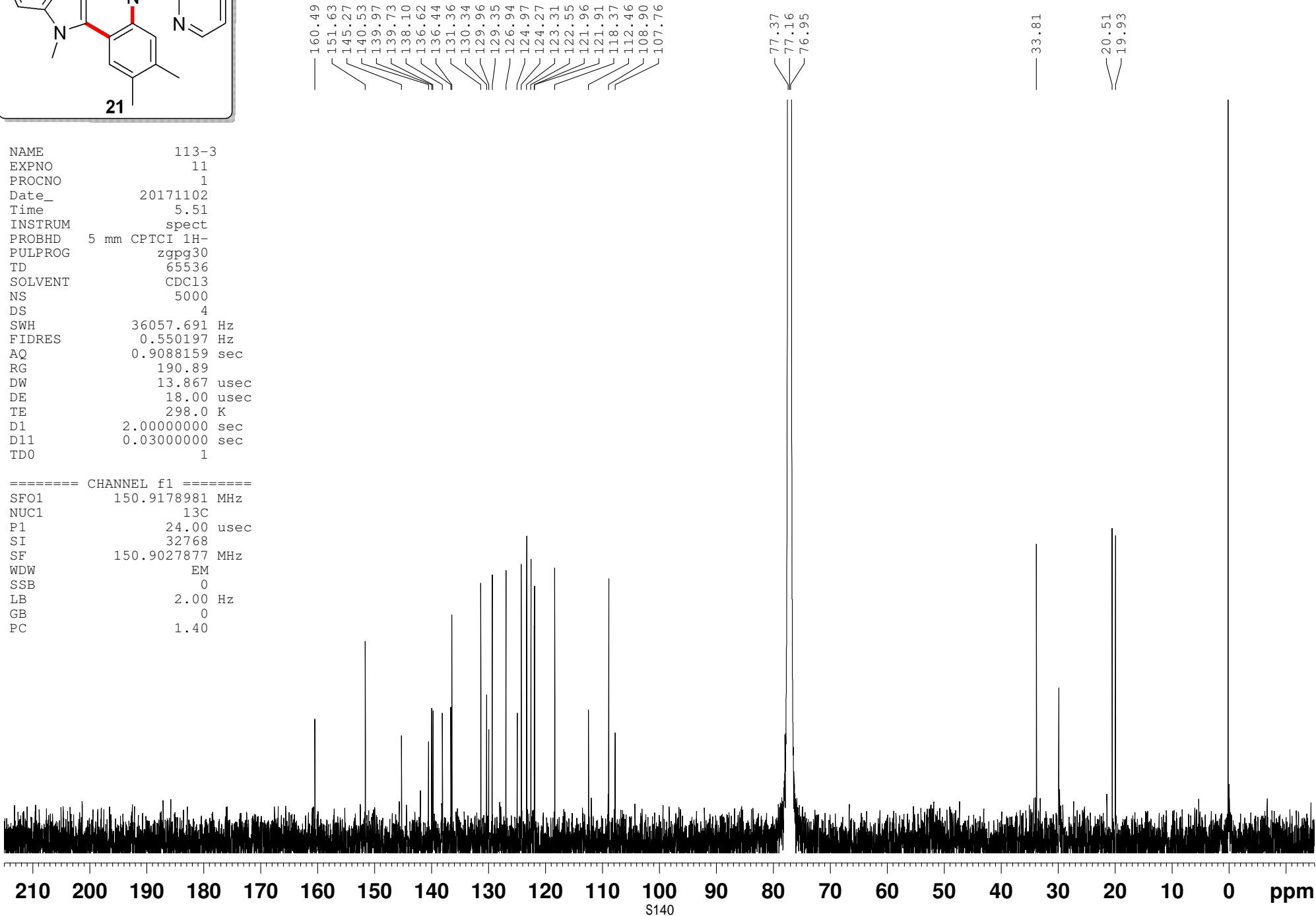


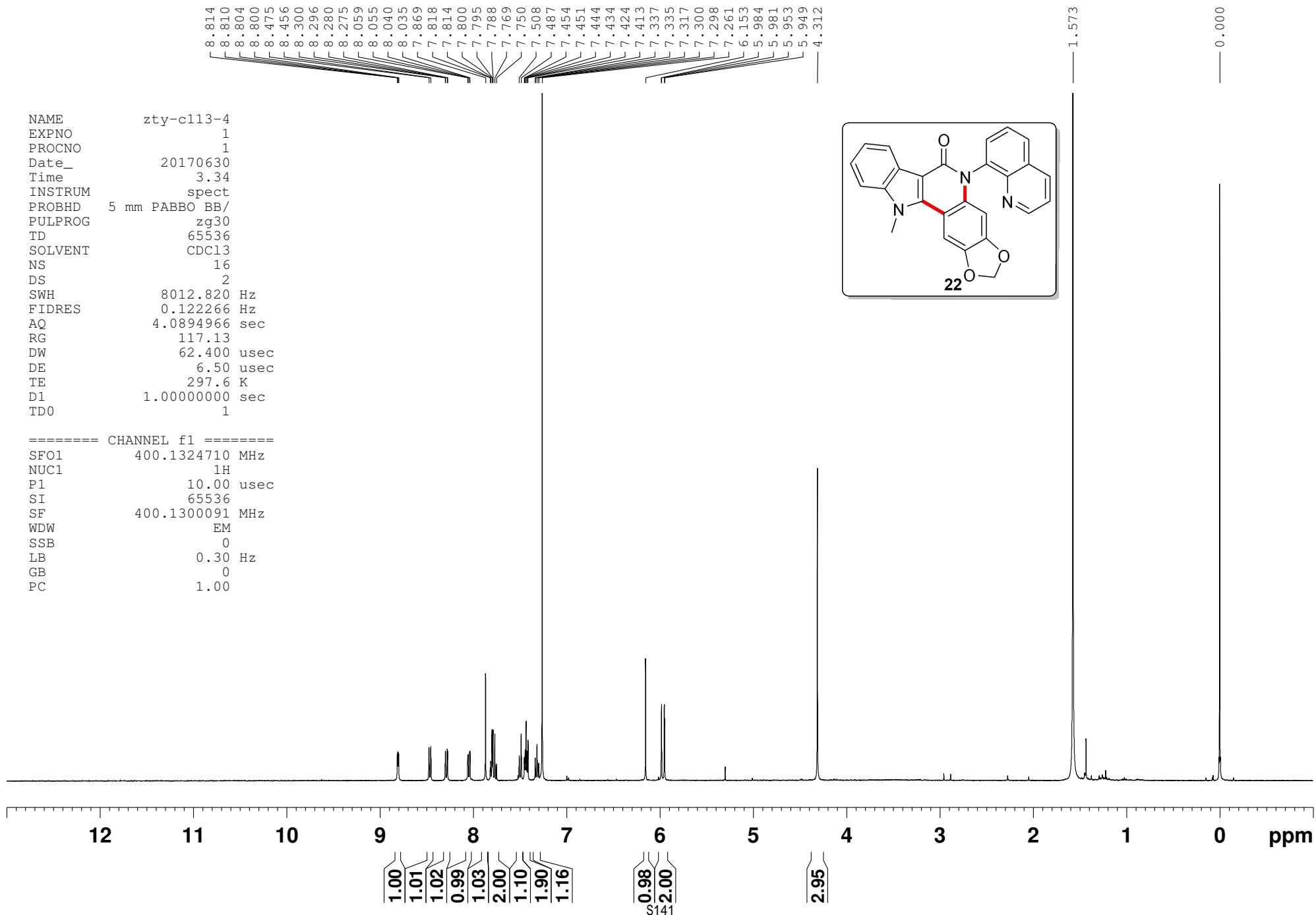


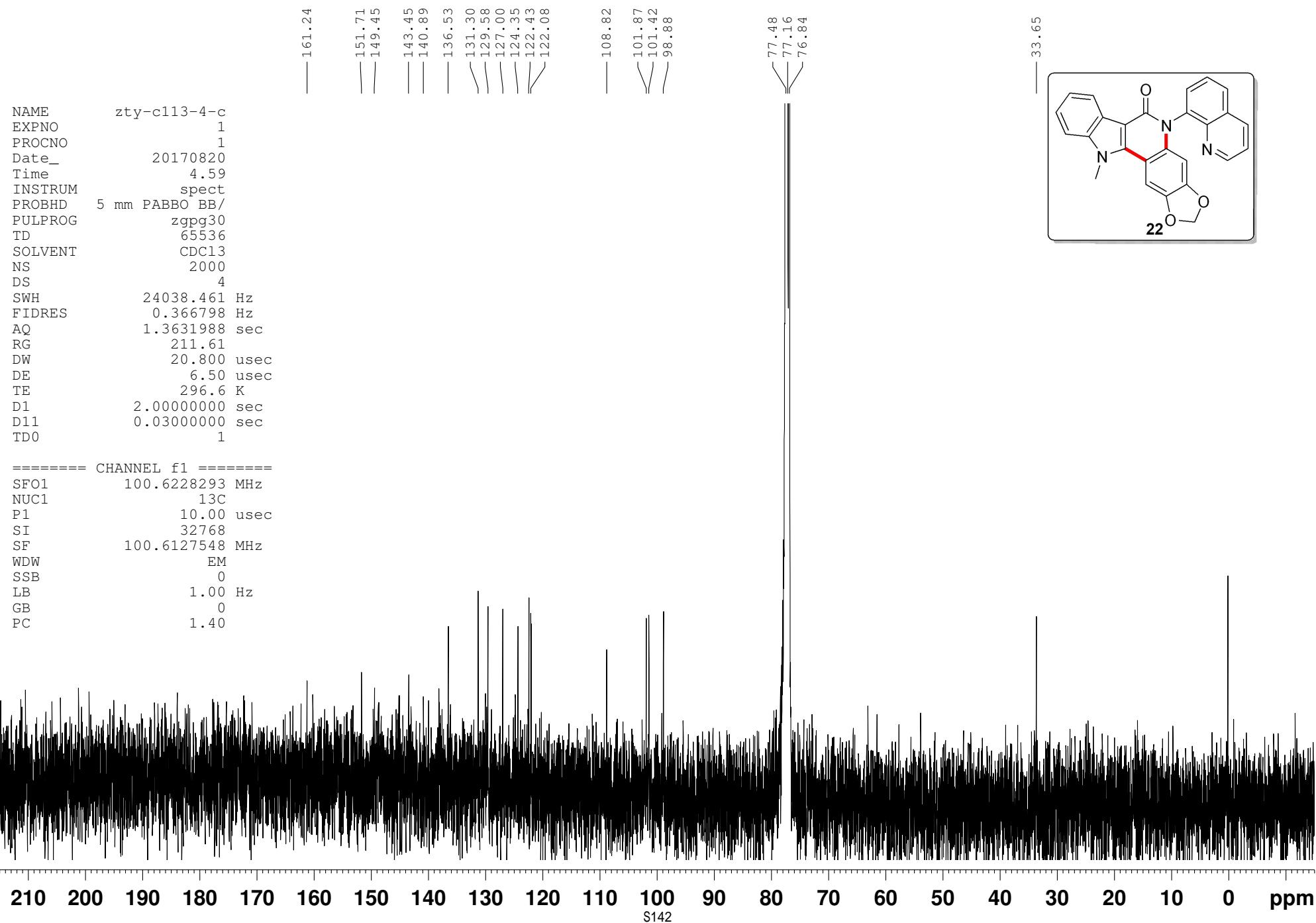


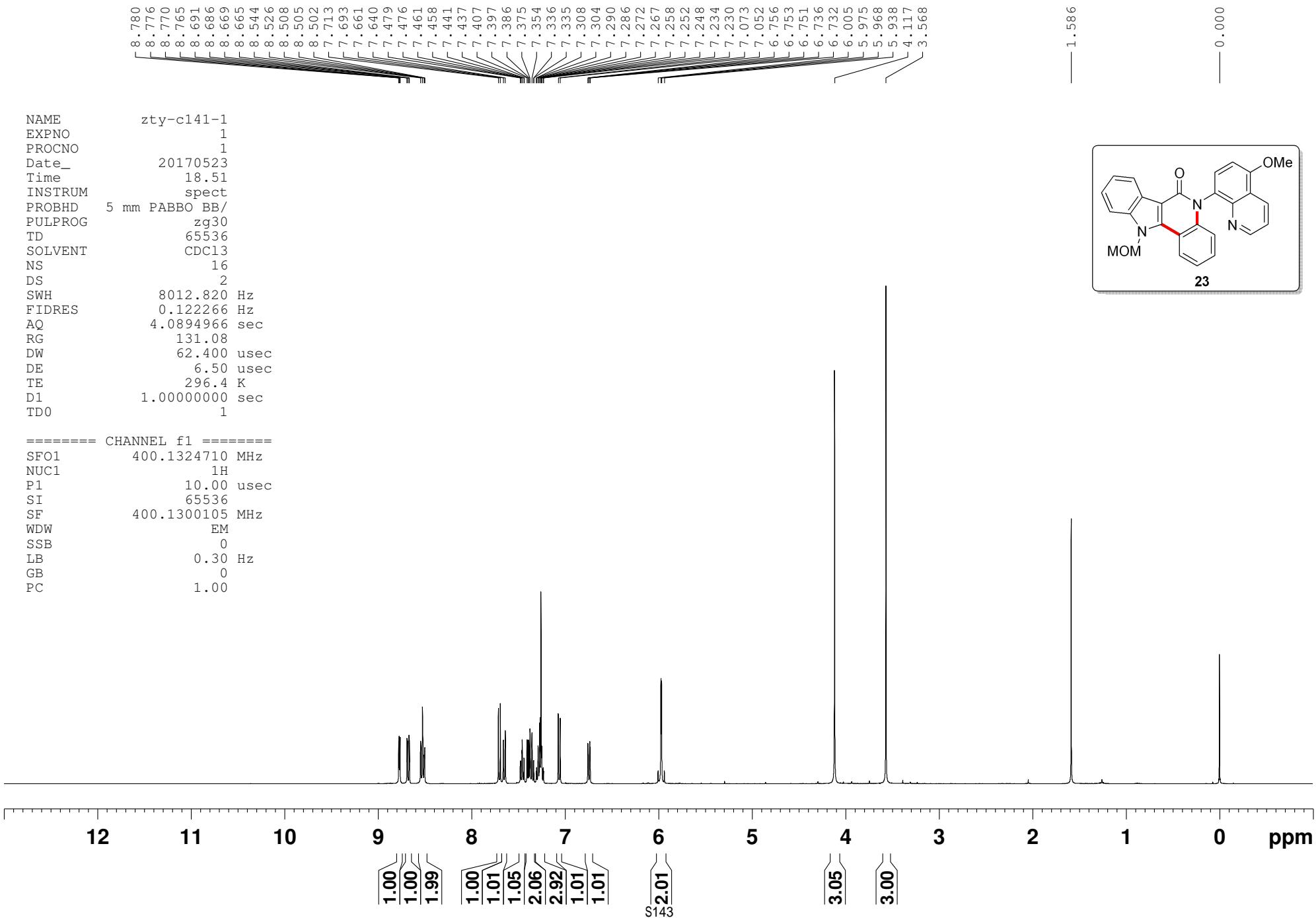
NAME 113-3
 EXPNO 11
 PROCNO 1
 Date_ 20171102
 Time 5.51
 INSTRUM spect
 PROBHD 5 mm CPTCI 1H-
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 5000
 DS 4
 SWH 36057.691 Hz
 FIDRES 0.550197 Hz
 AQ 0.9088159 sec
 RG 190.89
 DW 13.867 usec
 DE 18.00 usec
 TE 298.0 K
 D1 2.0000000 sec
 D11 0.0300000 sec
 TDO 1

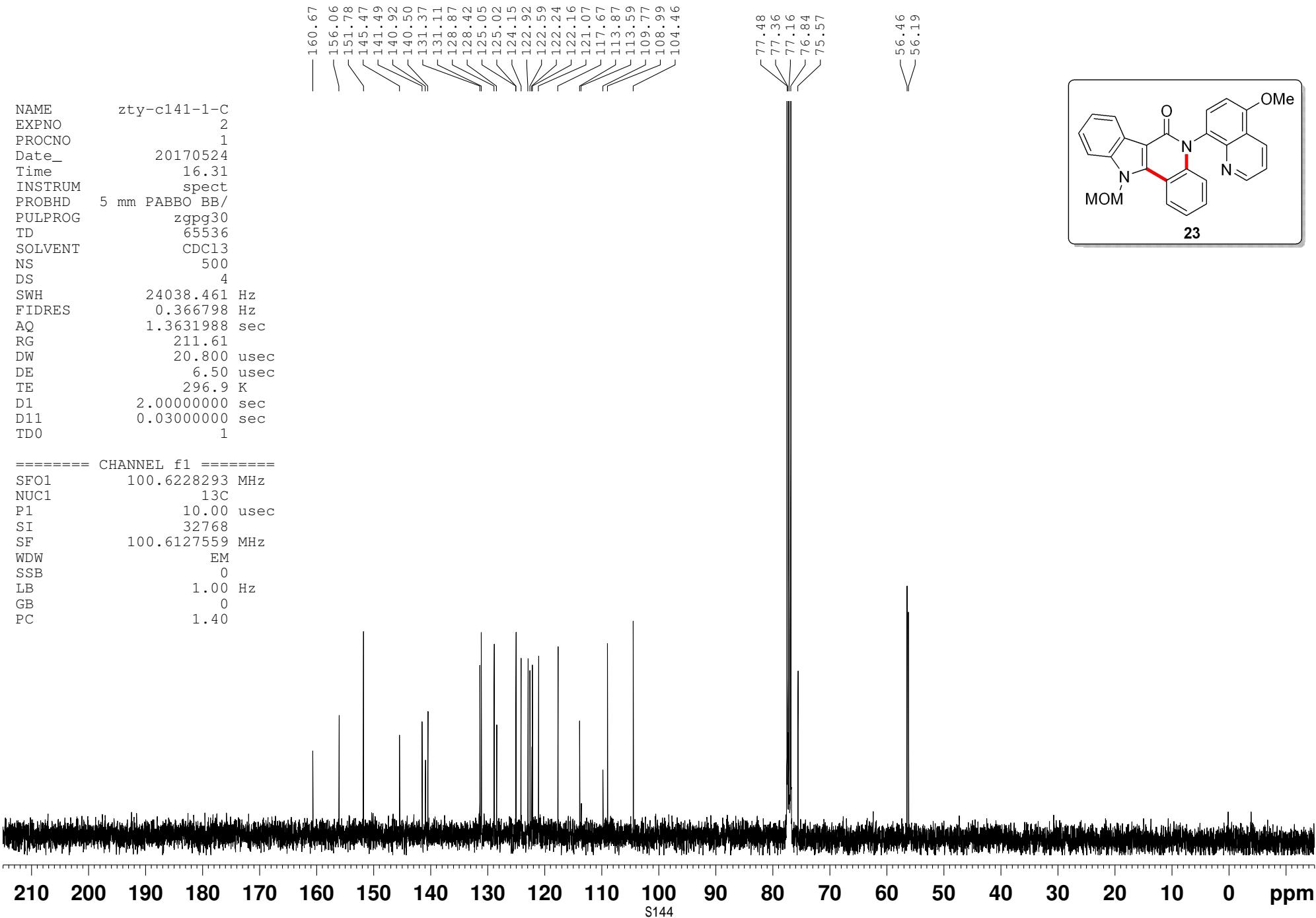
===== CHANNEL f1 ======
 SFO1 150.9178981 MHz
 NUC1 13C
 P1 24.00 usec
 SI 32768
 SF 150.9027877 MHz
 WDW EM
 SSB 0
 LB 2.00 Hz
 GB 0
 PC 1.40

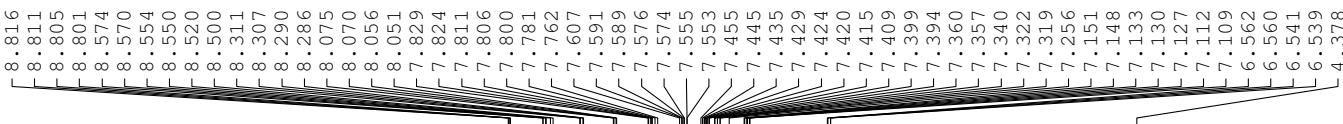






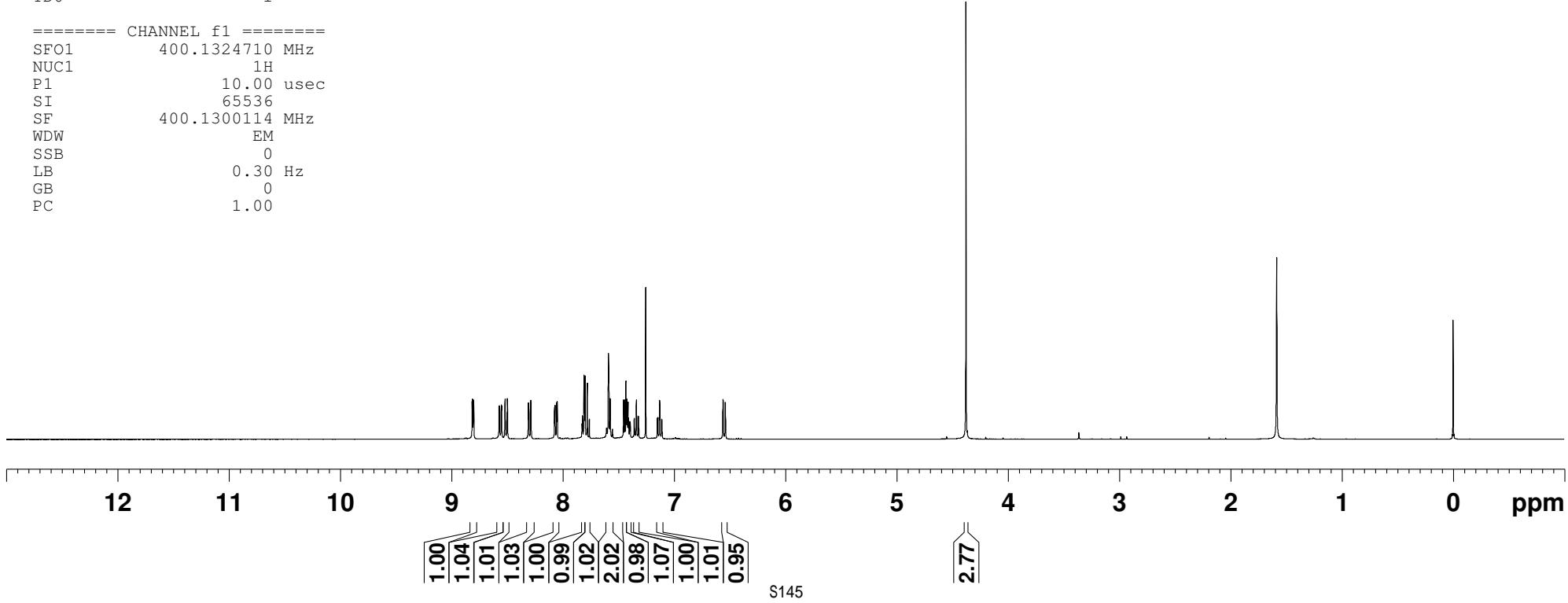
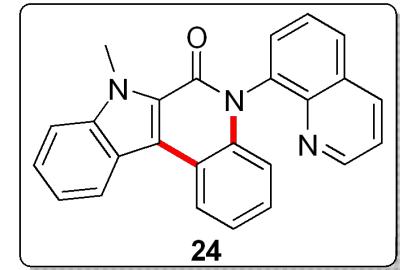






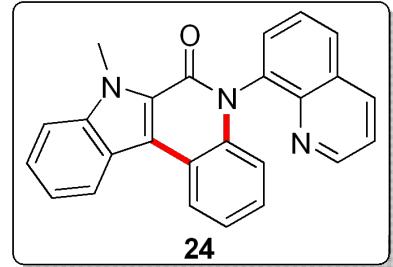
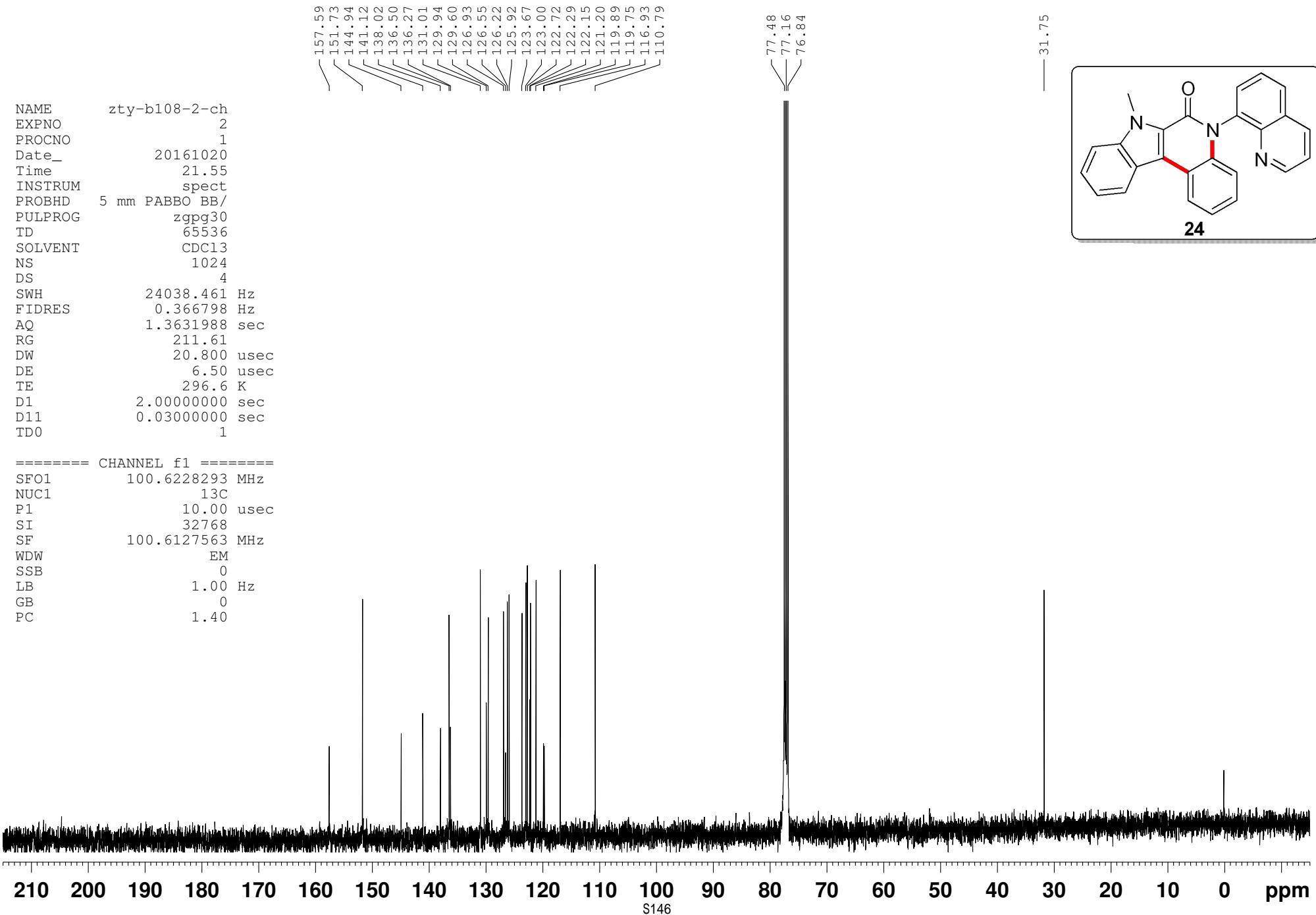
NAME zty-b108-2-ch
EXPNO 1
PROCNO 1
Date_ 20161020
Time 20.55
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl₃
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 82.9
DW 62.400 usec
DE 6.50 usec
TE 296.0 K
D1 1.00000000 sec
TD0 1

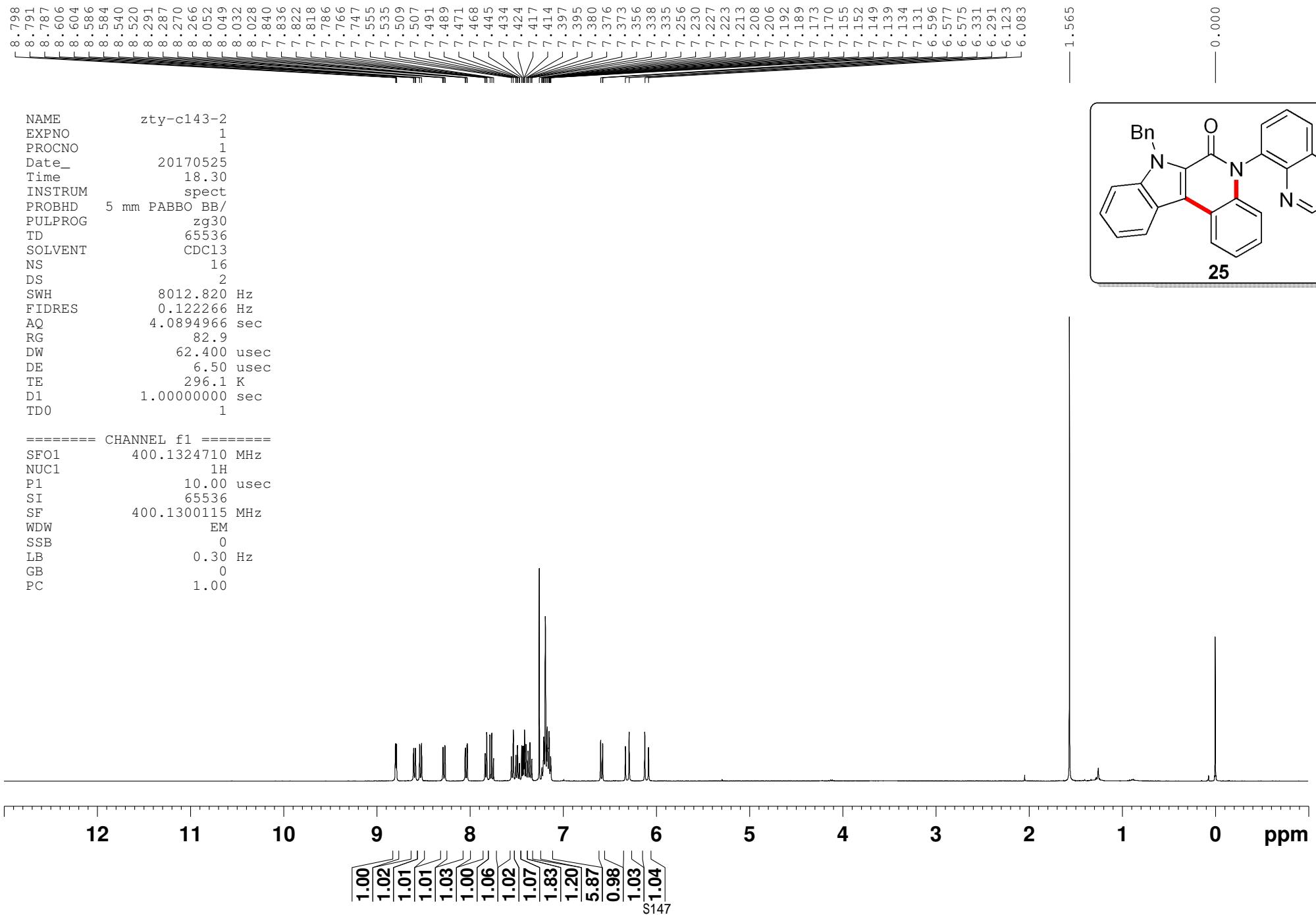
===== CHANNEL f1 =====
SFO1 400.1324710 MHz
NUC1 1H
P1 10.00 usec
SI 65536
SF 400.1300114 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



NAME zty-b108-2-ch
 EXPNO 2
 PROCNO 1
 Date_ 20161020
 Time 21.55
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 1024
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631988 sec
 RG 211.61
 DW 20.800 usec
 DE 6.50 usec
 TE 296.6 K
 D1 2.0000000 sec
 D11 0.0300000 sec
 TD0 1

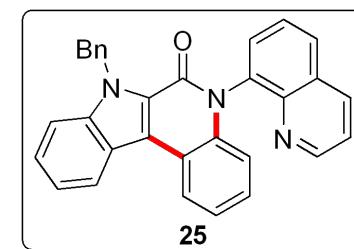
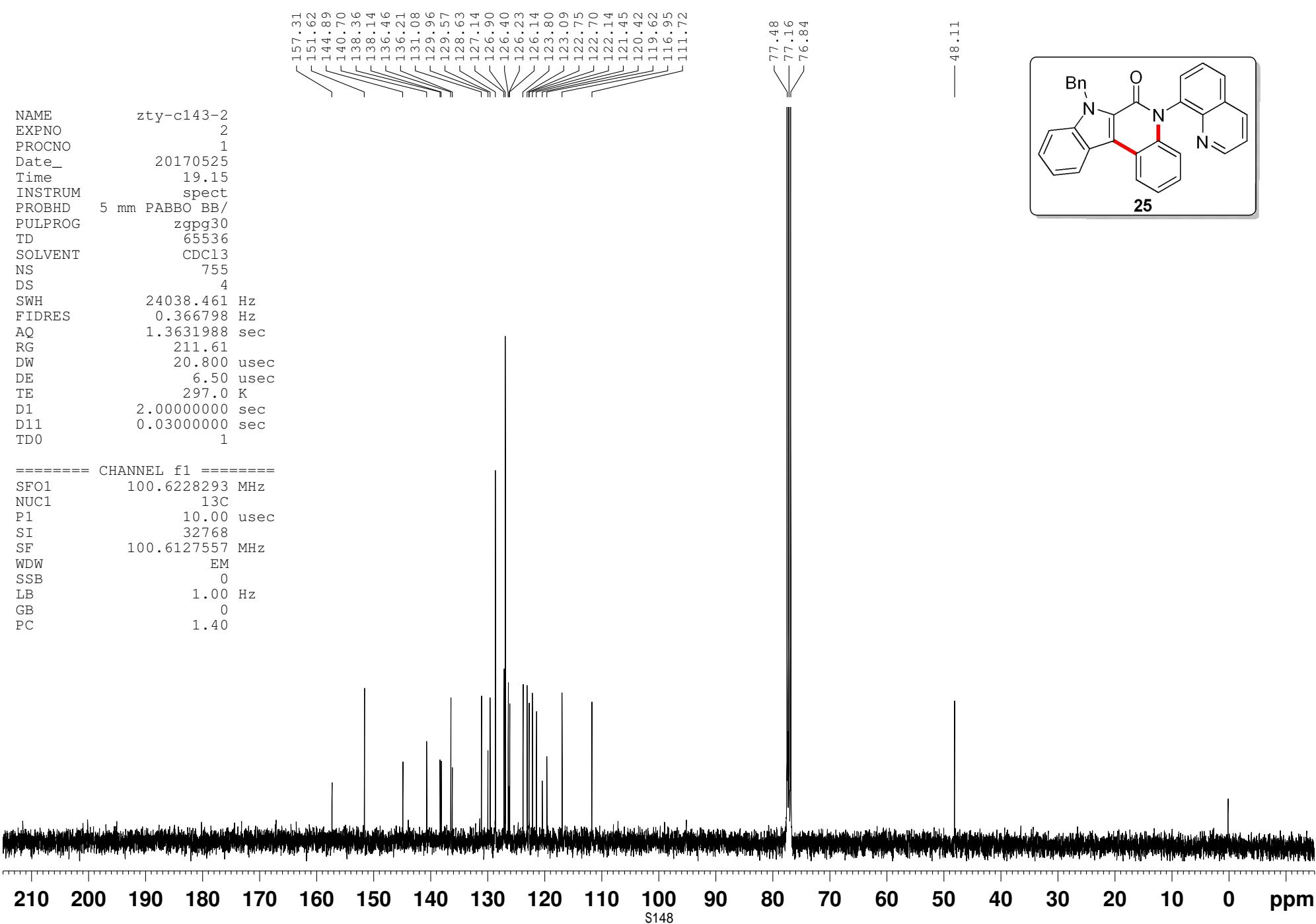
===== CHANNEL f1 =====
 SFO1 100.6228293 MHz
 NUC1 13C
 P1 10.00 usec
 SI 32768
 SF 100.6127563 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

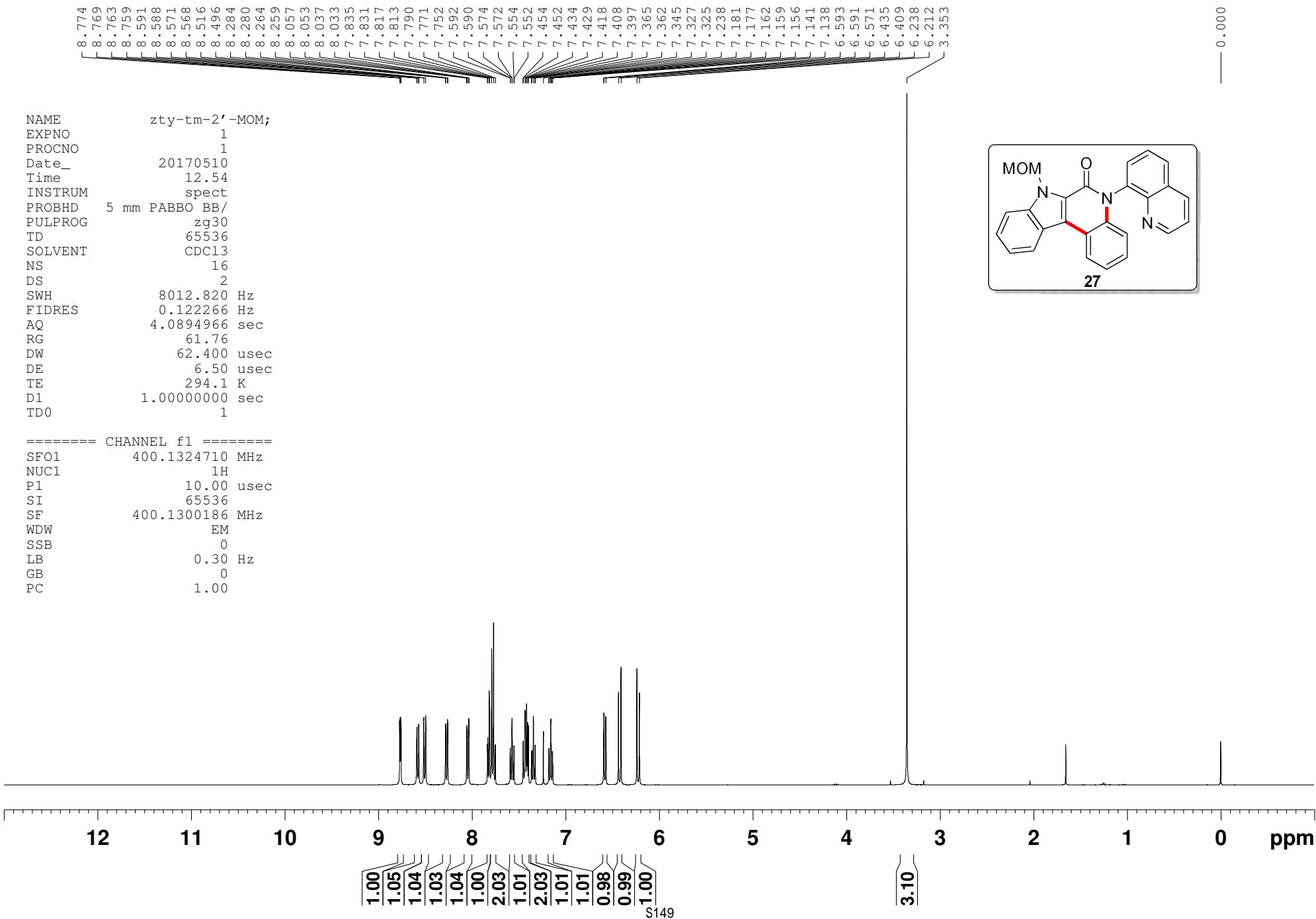




NAME zty-c143-2
 EXPNO 2
 PROCNO 1
 Date_ 20170525
 Time 19.15
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 755
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631988 sec
 RG 211.61
 DW 20.800 usec
 DE 6.50 usec
 TE 297.0 K
 D1 2.0000000 sec
 D11 0.03000000 sec
 TDO 1

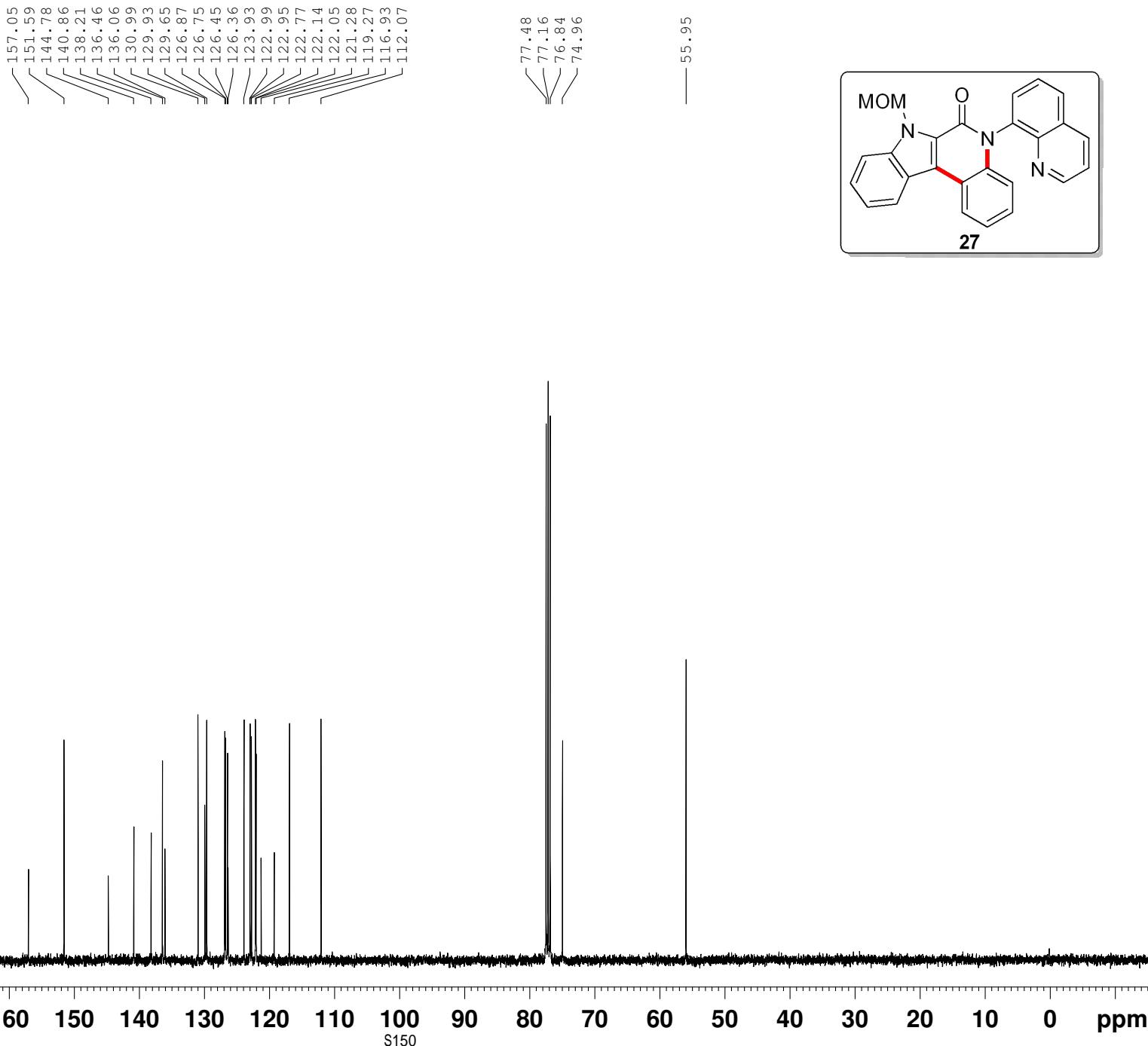
===== CHANNEL f1 =====
 SFO1 100.6228293 MHz
 NUC1 13C
 P1 10.00 usec
 SI 32768
 SF 100.6127557 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

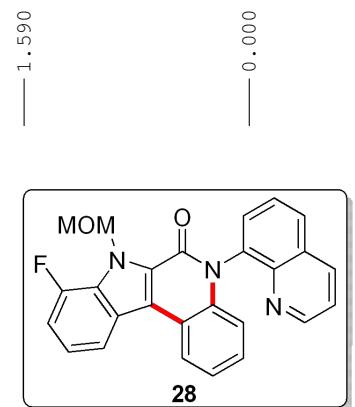
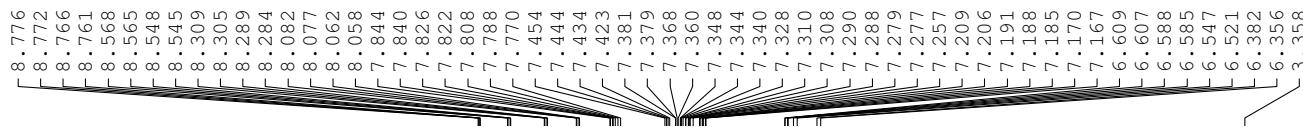




NAME zty-tm-2;
 EXPNO 2
 PROCNO 1
 Date_ 20170510
 Time 13.10
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 256
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631988 sec
 RG 211.61
 DW 20.800 usec
 DE 6.50 usec
 TE 295.0 K
 D1 2.0000000 sec
 D11 0.0300000 sec
 TDO 1

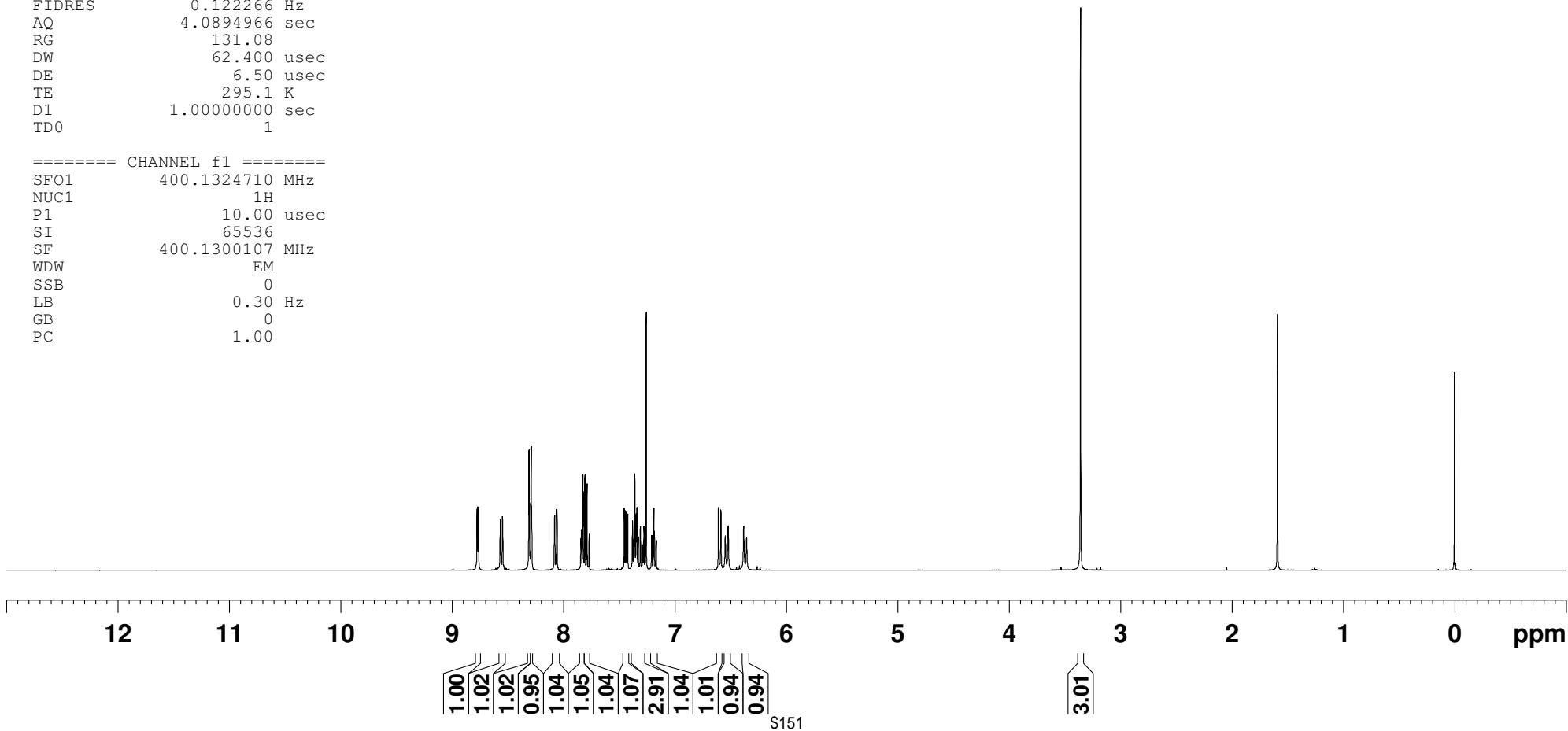
===== CHANNEL f1 =====
 SFO1 100.6228293 MHz
 NUC1 13C
 P1 10.00 usec
 SI 32768
 SF 100.6127614 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40





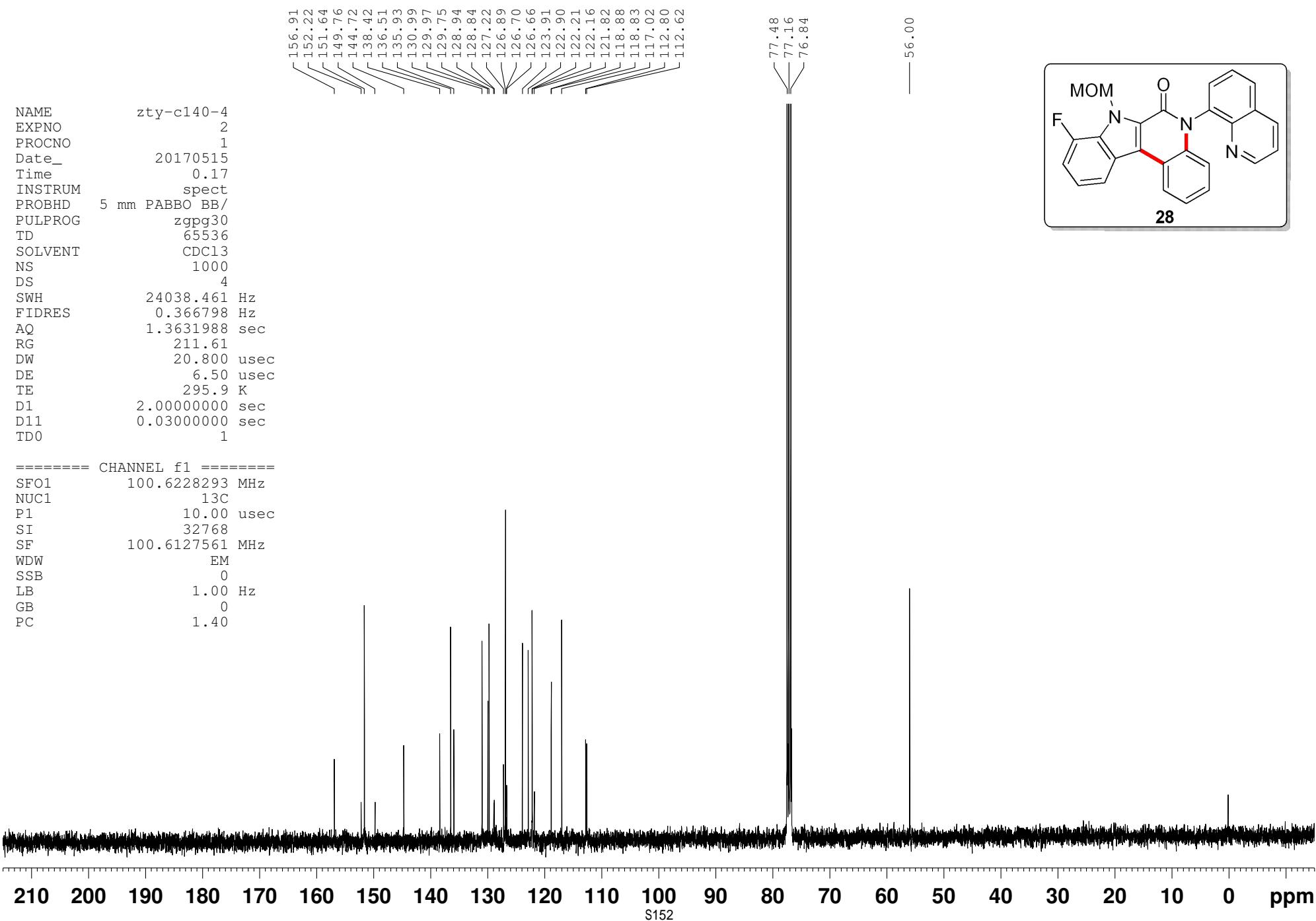
NAME zty-c140-4
 EXPNO 1
 PROCNO 1
 Date_ 20170514
 Time 23.19
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zg30
 TD 65536
 SOLVENT CDCl₃
 NS 16
 DS 2
 SWH 8012.820 Hz
 FIDRES 0.122266 Hz
 AQ 4.0894966 sec
 RG 131.08
 DW 62.400 usec
 DE 6.50 usec
 TE 295.1 K
 D1 1.00000000 sec
 TDO 1

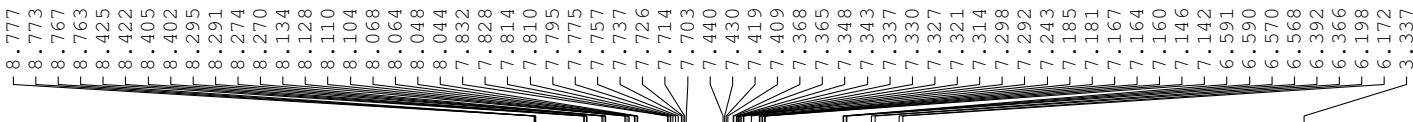
===== CHANNEL f1 ======
 SFO1 400.1324710 MHz
 NUC1 1H
 P1 10.00 usec
 SI 65536
 SF 400.1300107 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



NAME zty-c140-4
 EXPNO 2
 PROCNO 1
 Date_ 20170515
 Time 0.17
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 1000
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631988 sec
 RG 211.61
 DW 20.800 usec
 DE 6.50 usec
 TE 295.9 K
 D1 2.0000000 sec
 D11 0.0300000 sec
 TDO 1

===== CHANNEL f1 =====
 SFO1 100.6228293 MHz
 NUC1 13C
 P1 10.00 usec
 SI 32768
 SF 100.6127561 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

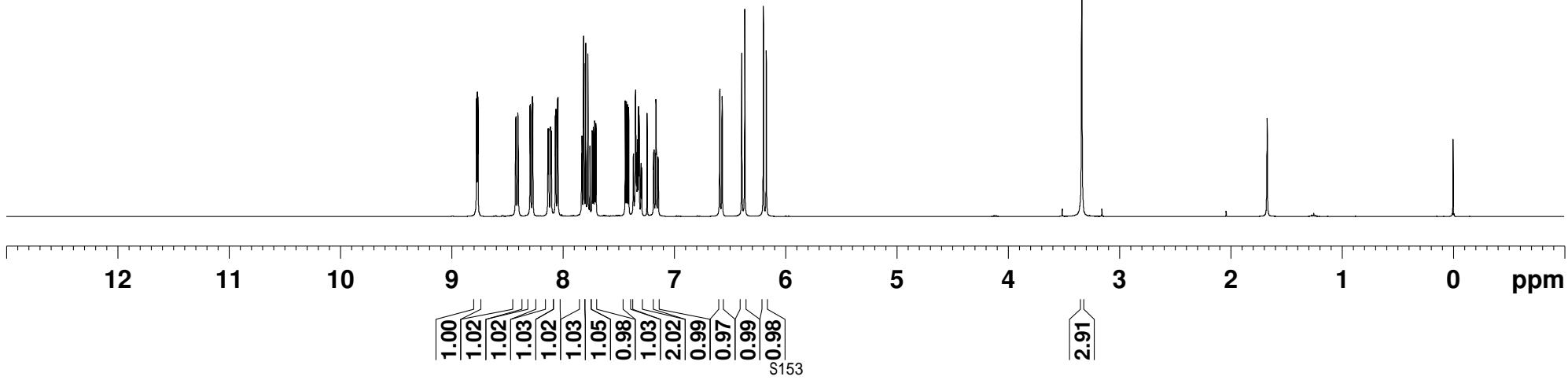
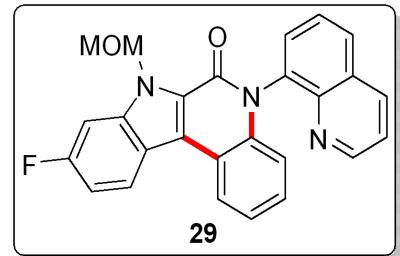




0.000

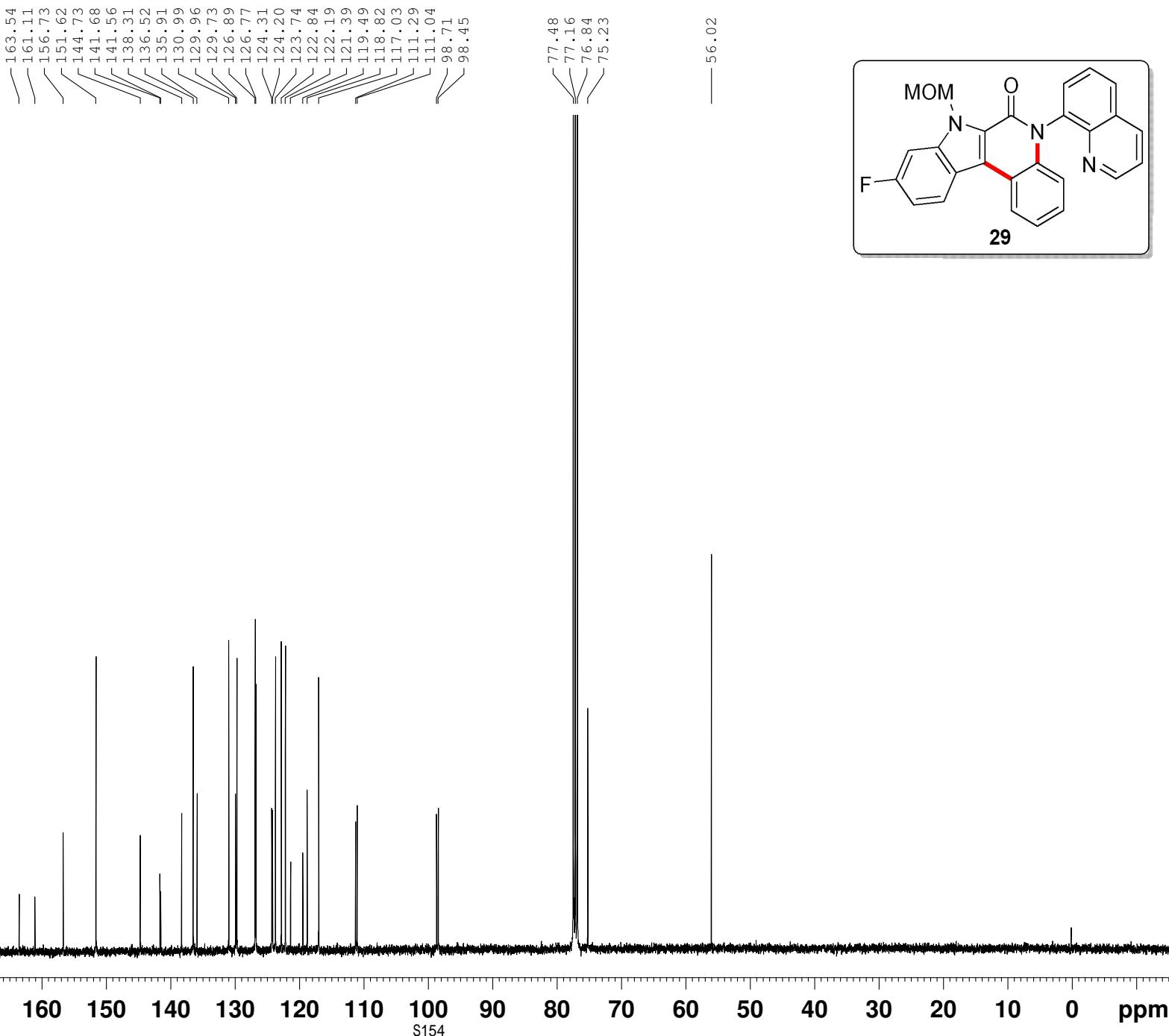
NAME zty-c140-3
EXPNO 1
PROCNO 1
Date_ 20170513
Time 11.27
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl₃
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 61.76
DW 62.400 usec
DE 6.50 usec
TE 294.1 K
D1 1.00000000 sec
TD0 1

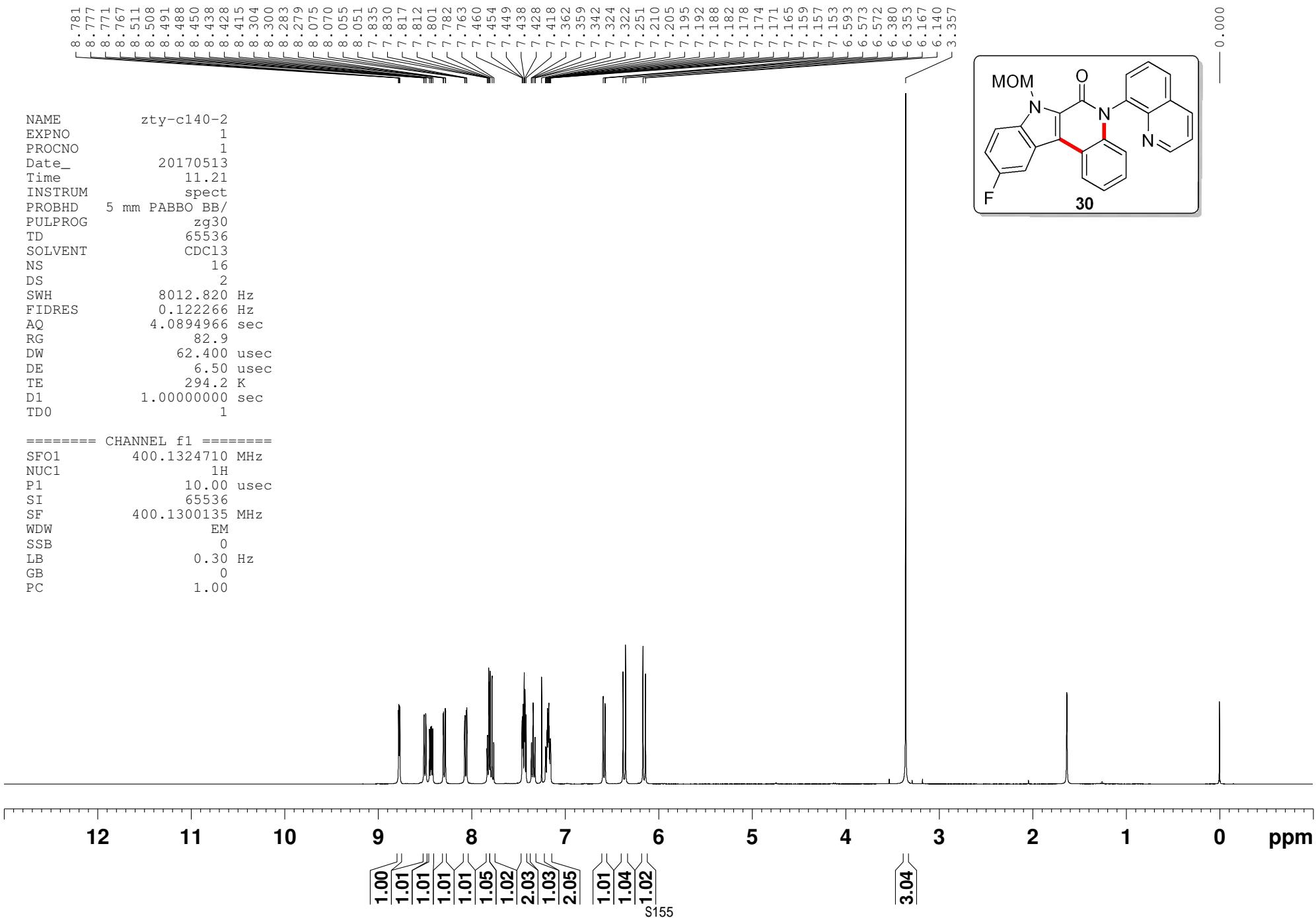
===== CHANNEL f1 ======
SFO1 400.1324710 MHz
NUC1 1H
P1 10.00 usec
SI 65536
SF 400.1300166 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



NAME zty-c140-3
 EXPNO 2
 PROCNO 1
 Date_ 20170515
 Time 5.45
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 1024
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631988 sec
 RG 211.61
 DW 20.800 usec
 DE 6.50 usec
 TE 295.7 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

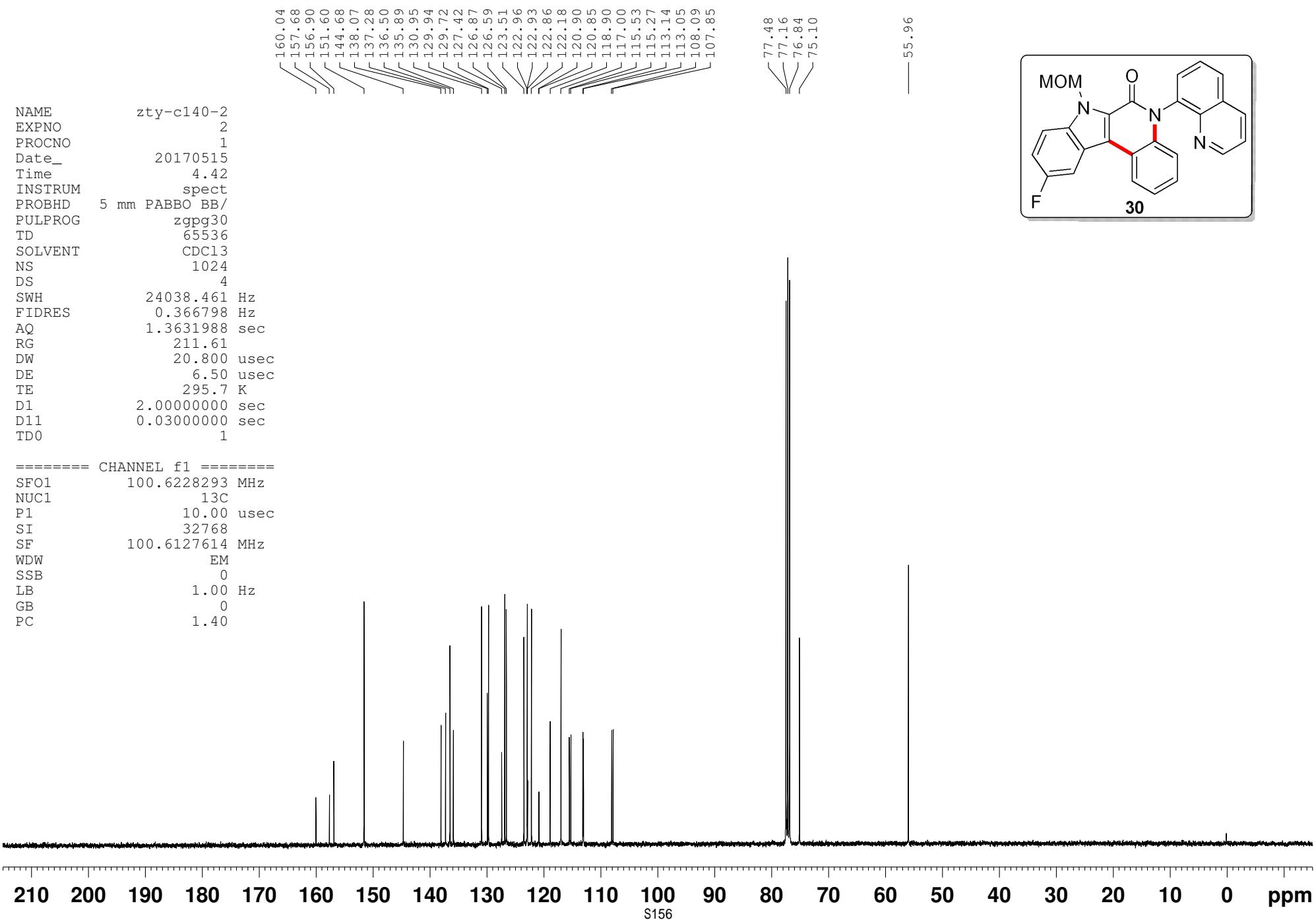
===== CHANNEL f1 =====
 SFO1 100.6228293 MHz
 NUC1 13C
 P1 10.00 usec
 SI 32768
 SF 100.6127591 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

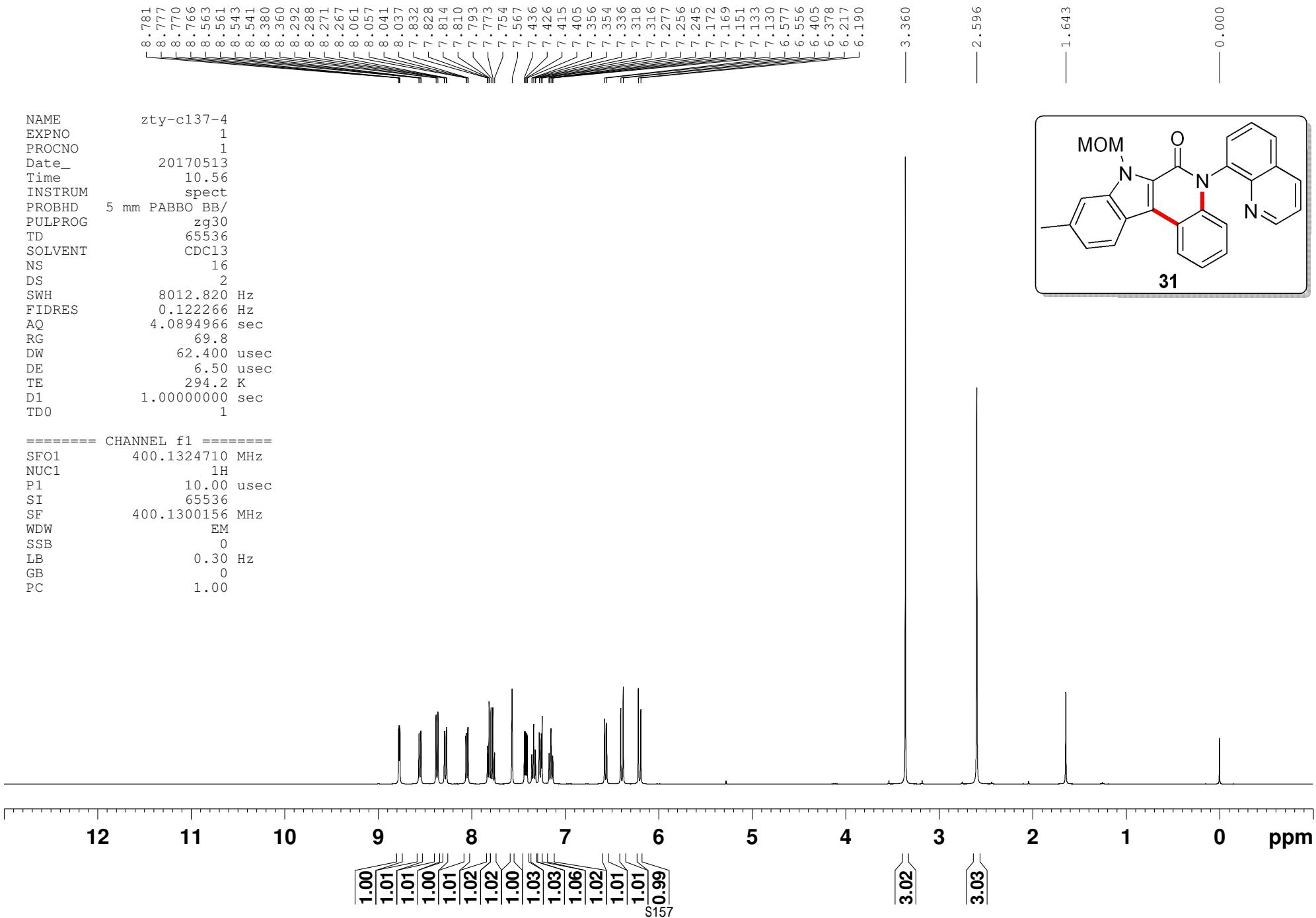




NAME zty-c140-2
 EXPNO 2
 PROCNO 1
 Date_ 20170515
 Time 4.42
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 1024
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631988 sec
 RG 211.61
 DW 20.800 usec
 DE 6.50 usec
 TE 295.7 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TDO 1

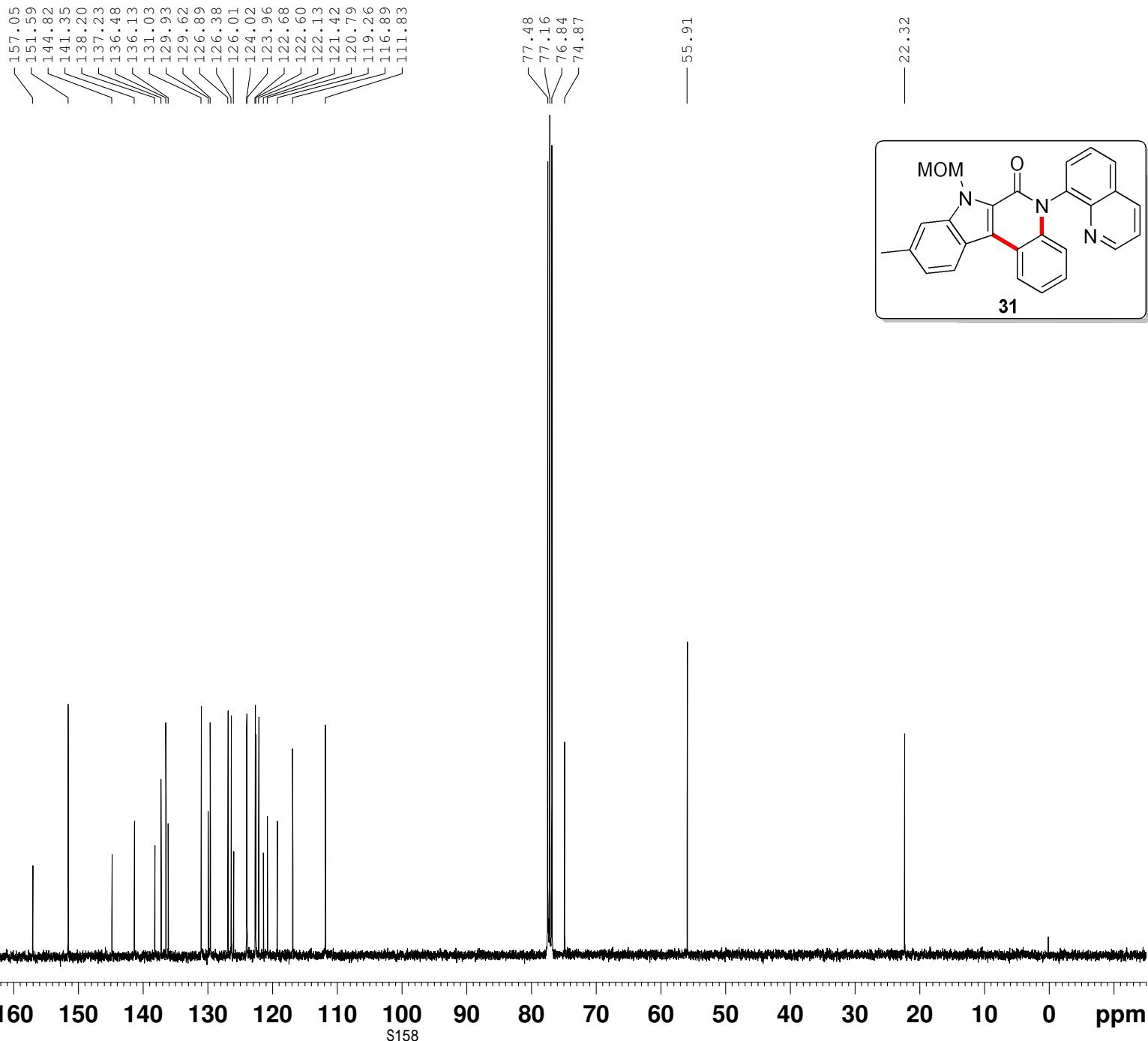
===== CHANNEL f1 =====
 SFO1 100.6228293 MHz
 NUC1 13C
 P1 10.00 usec
 SI 32768
 SF 100.6127614 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

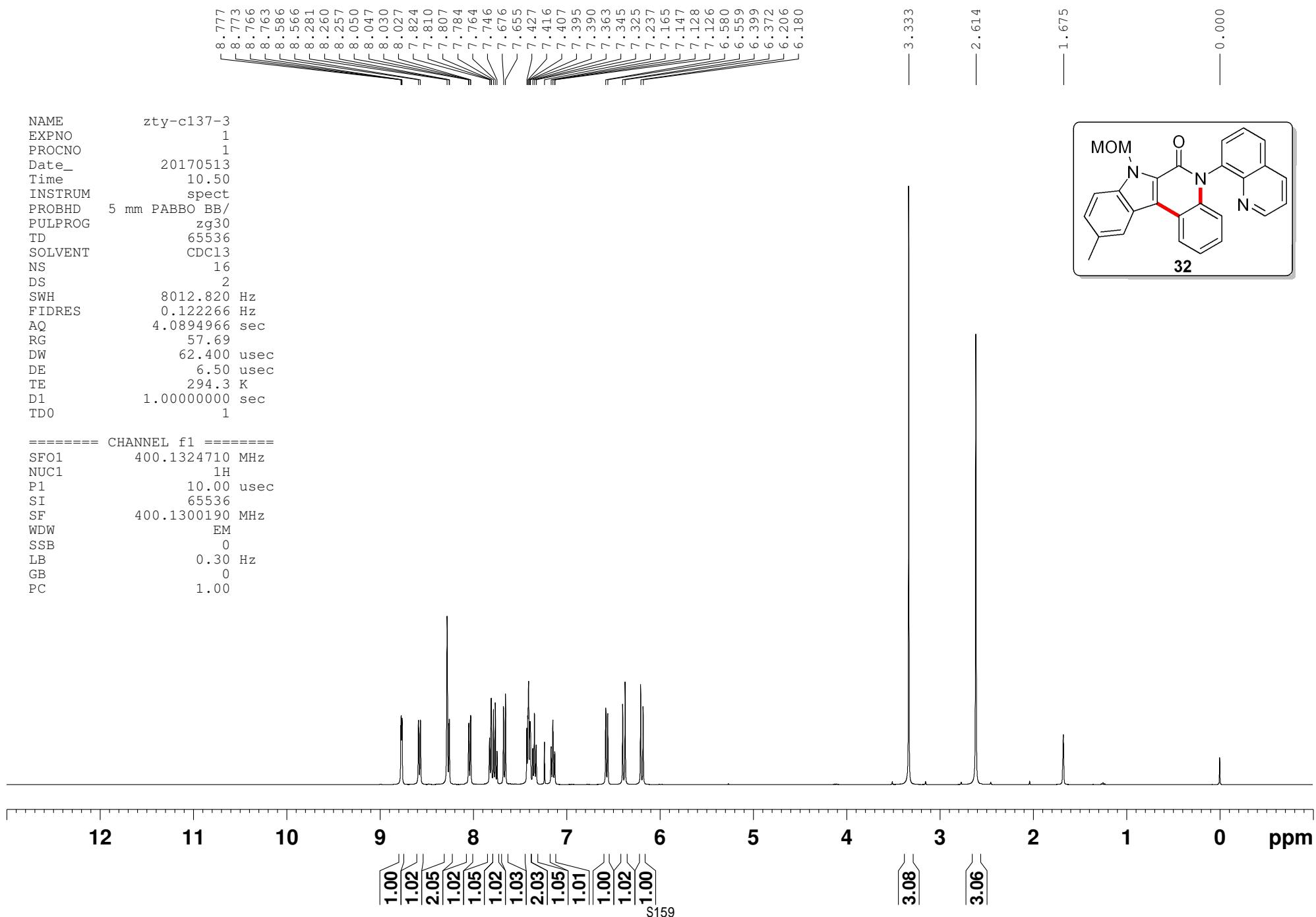




NAME zty-c137-4
 EXPNO 2
 PROCNO 1
 Date_ 20170515
 Time 3.03
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 500
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631988 sec
 RG 211.61
 DW 20.800 usec
 DE 6.50 usec
 TE 295.7 K
 D1 2.0000000 sec
 D11 0.0300000 sec
 TDO 1

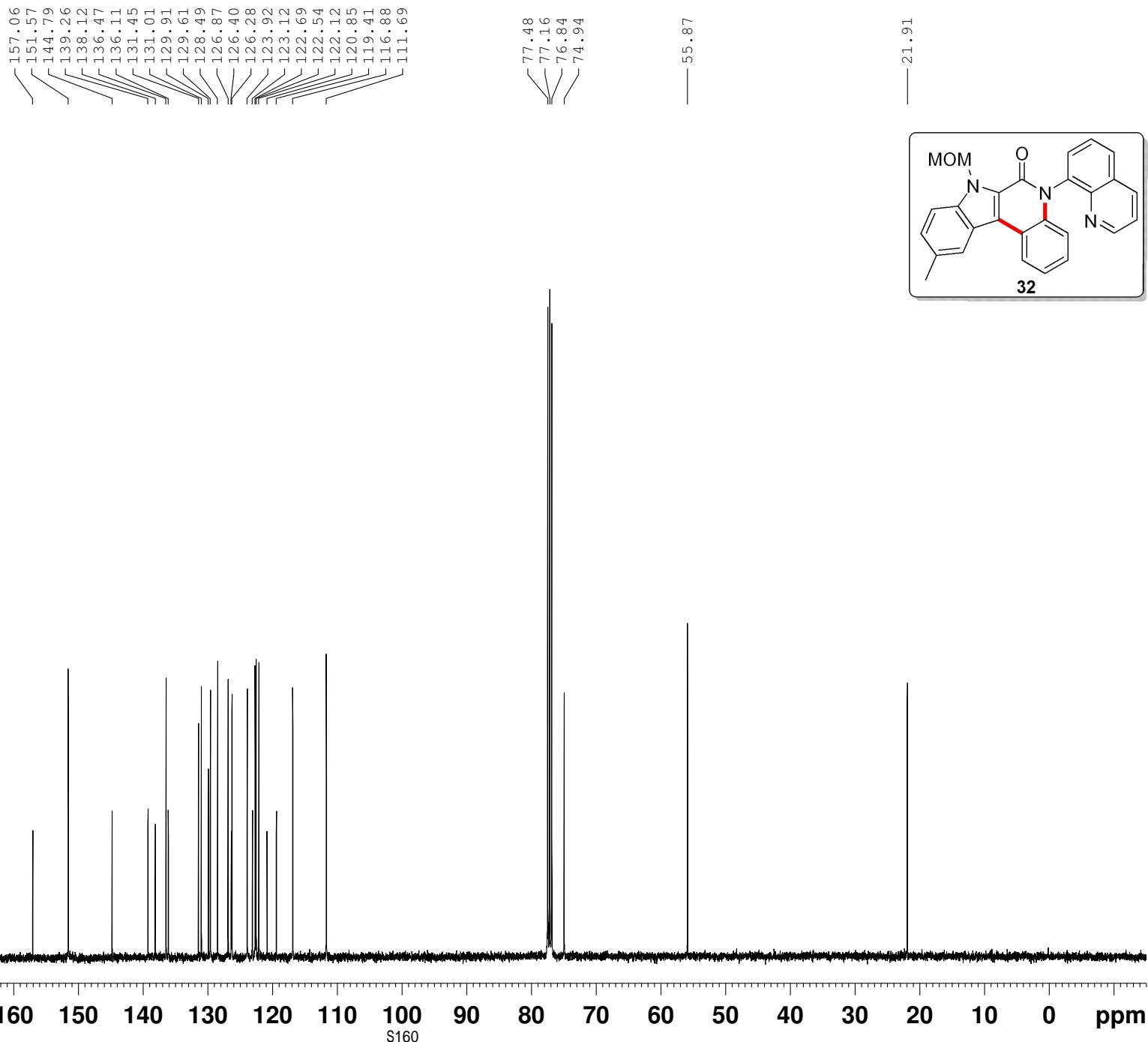
===== CHANNEL f1 =====
 SFO1 100.6228293 MHz
 NUC1 13C
 P1 10.00 usec
 SI 32768
 SF 100.6127600 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

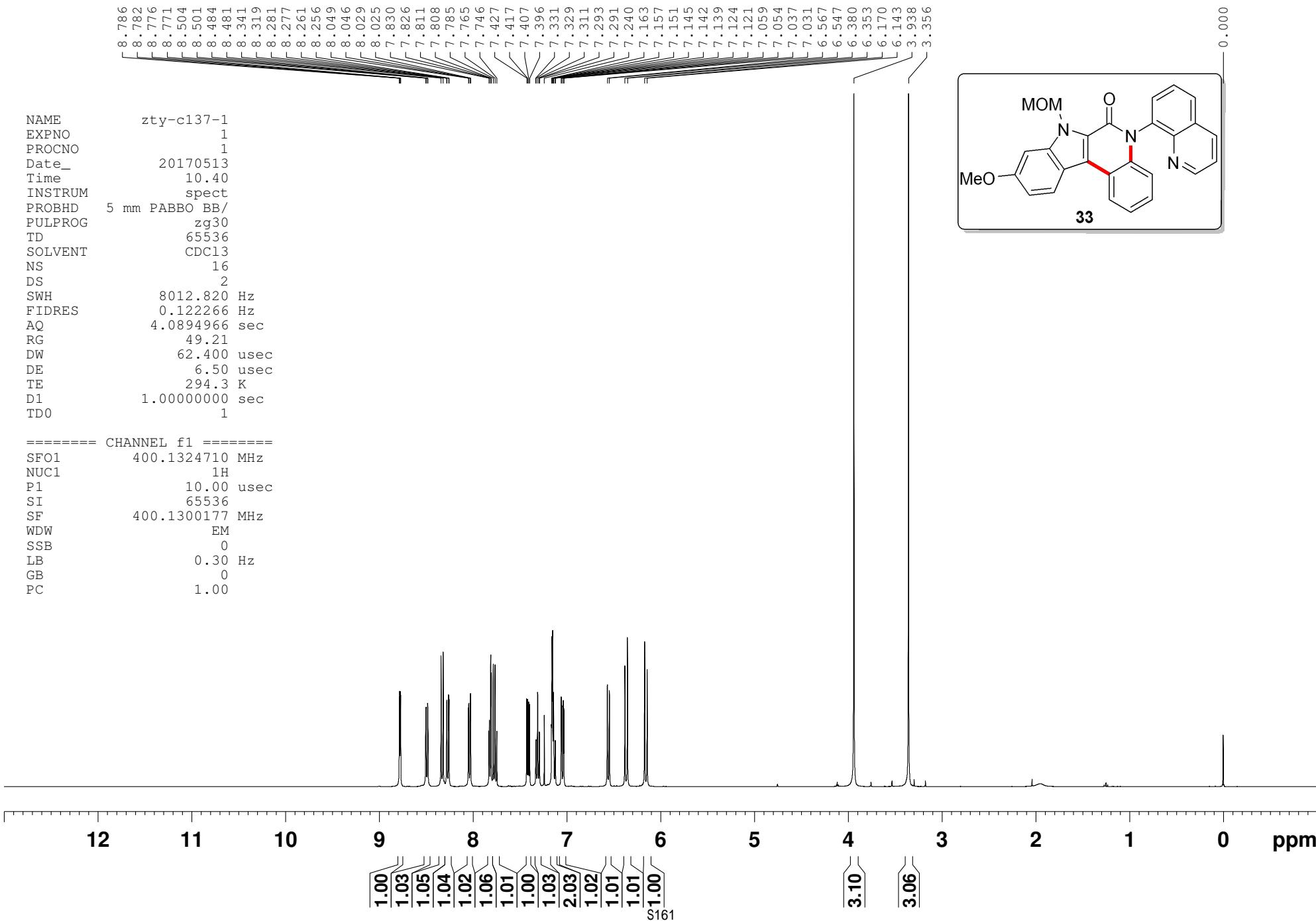




NAME zty-c137-3
 EXPNO 2
 PROCNO 1
 Date_ 20170515
 Time 2.30
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 500
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631988 sec
 RG 211.61
 DW 20.800 usec
 DE 6.50 usec
 TE 295.7 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TDO 1

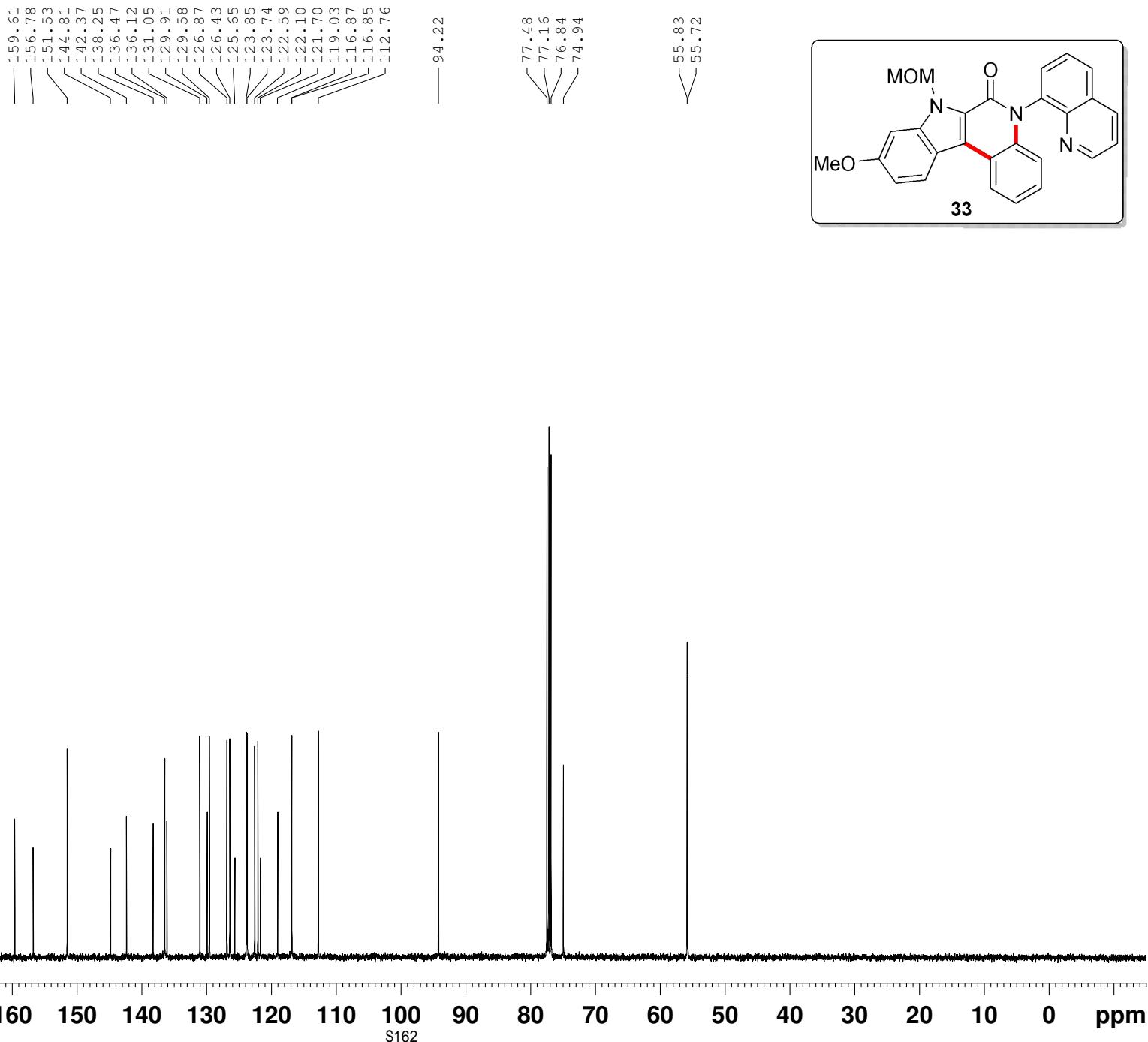
===== CHANNEL f1 =====
 SFO1 100.6228293 MHz
 NUC1 13C
 P1 10.00 usec
 SI 32768
 SF 100.6127623 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

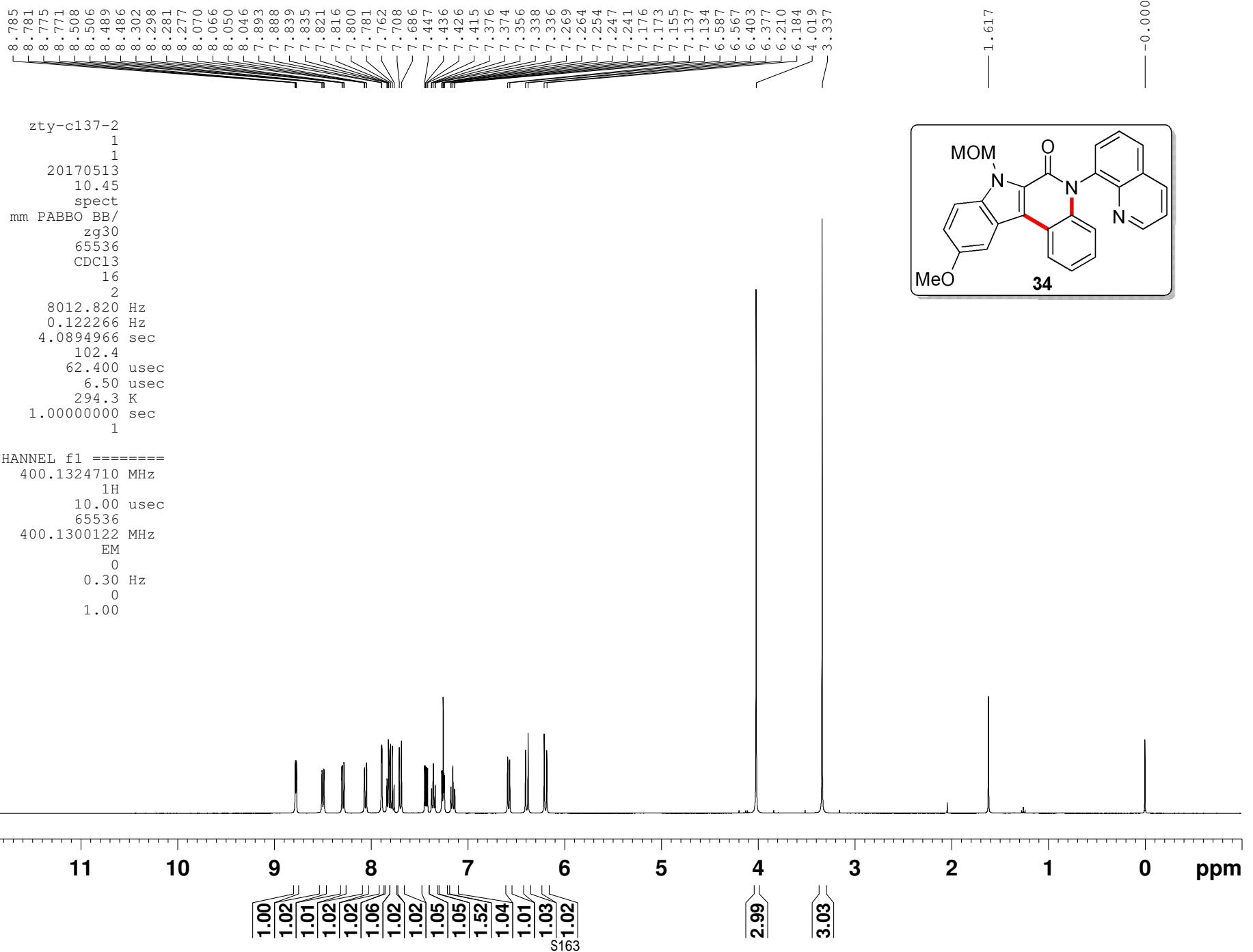




NAME zty-c137-1
 EXPNO 2
 PROCNO 1
 Date_ 20170515
 Time 1.25
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 500
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631988 sec
 RG 211.61
 DW 20.800 usec
 DE 6.50 usec
 TE 295.6 K
 D1 2.0000000 sec
 D11 0.03000000 sec
 TDO 1

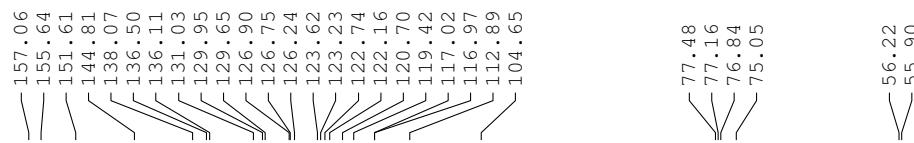
===== CHANNEL f1 =====
 SFO1 100.6228293 MHz
 NUC1 13C
 P1 10.00 usec
 SI 32768
 SF 100.6127630 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40





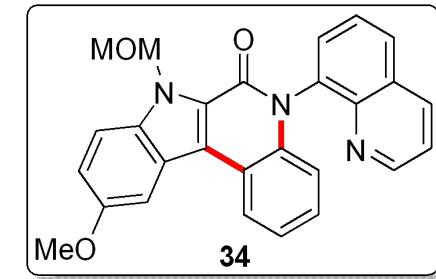
NAME zty-c137-2
 EXPNO 2
 PROCNO 1
 Date_ 20170515
 Time 1.58
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 500
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631988 sec
 RG 211.61
 DW 20.800 usec
 DE 6.50 usec
 TE 295.7 K
 D1 2.0000000 sec
 D11 0.0300000 sec
 TD0 1

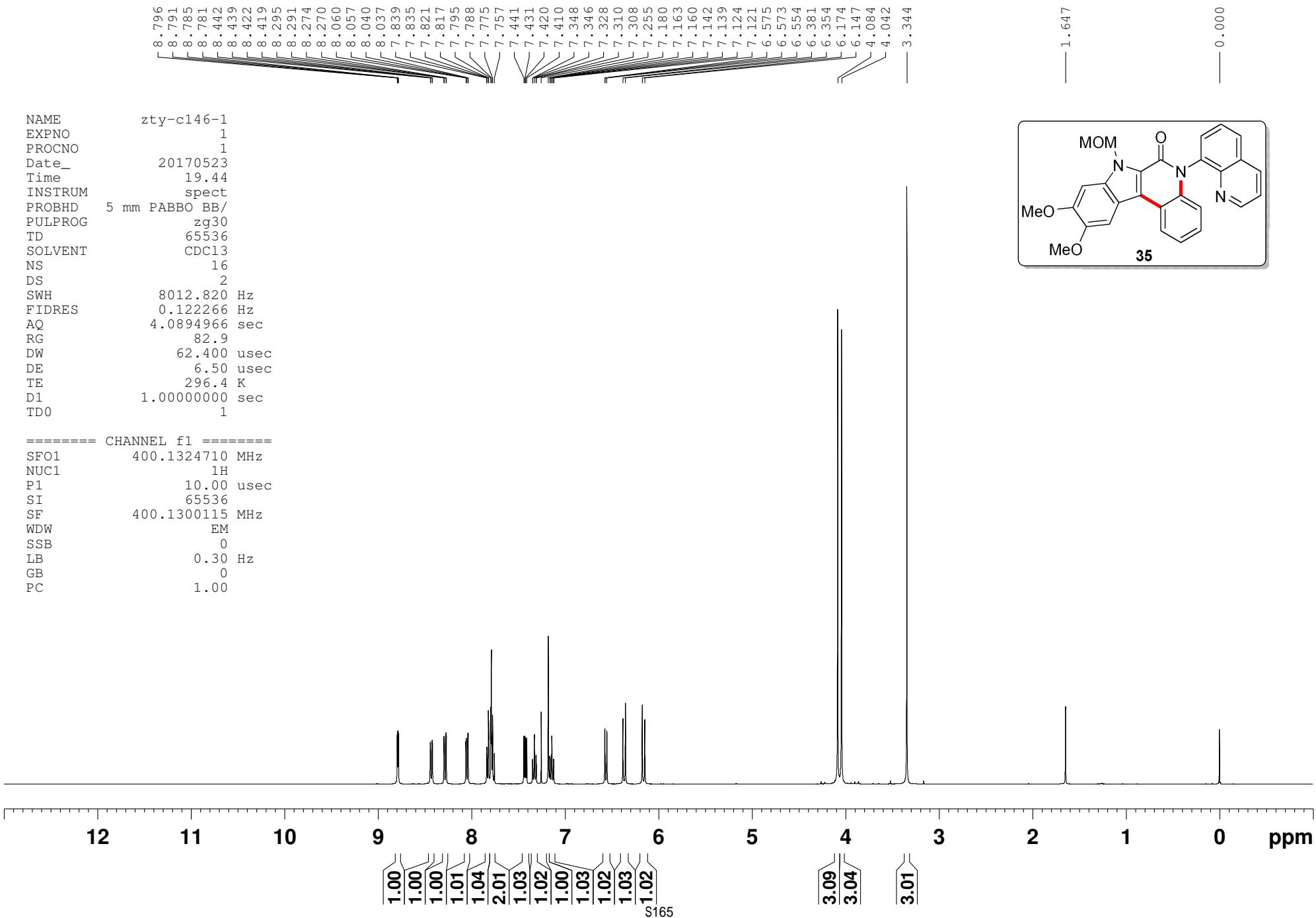
===== CHANNEL f1 =====
 SFO1 100.6228293 MHz
 NUC1 13C
 P1 10.00 usec
 SI 32768
 SF 100.6127579 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

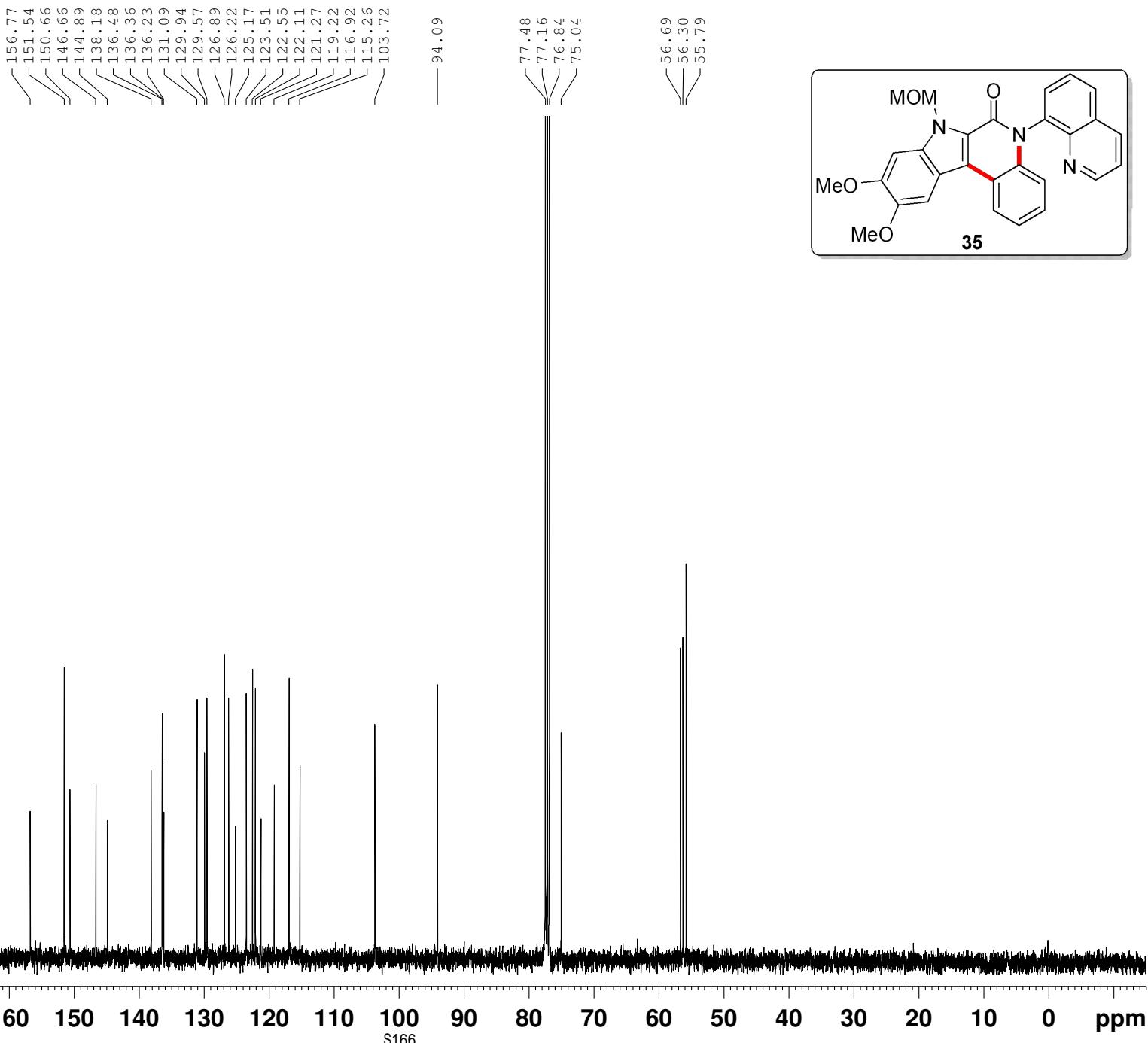
S164

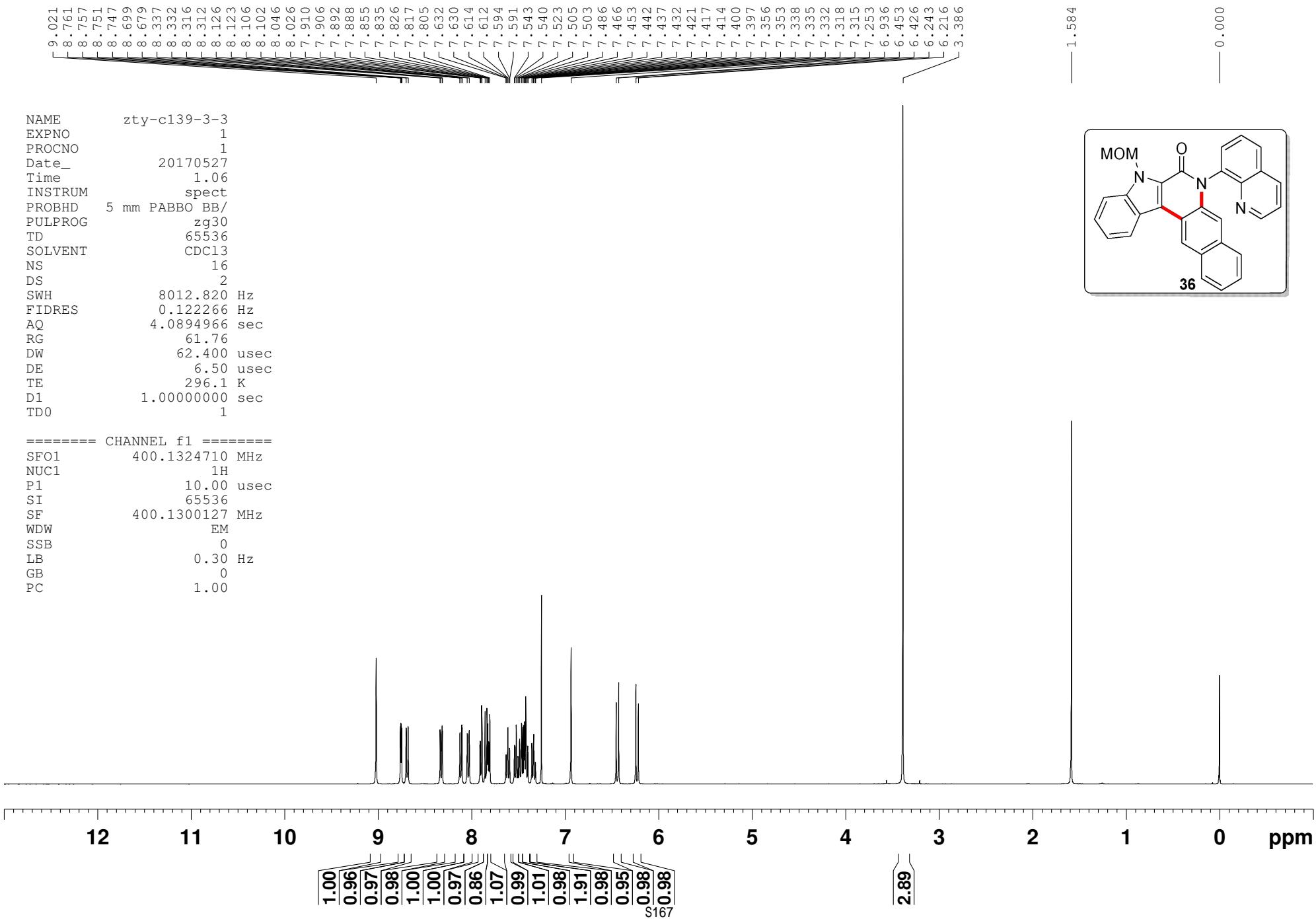


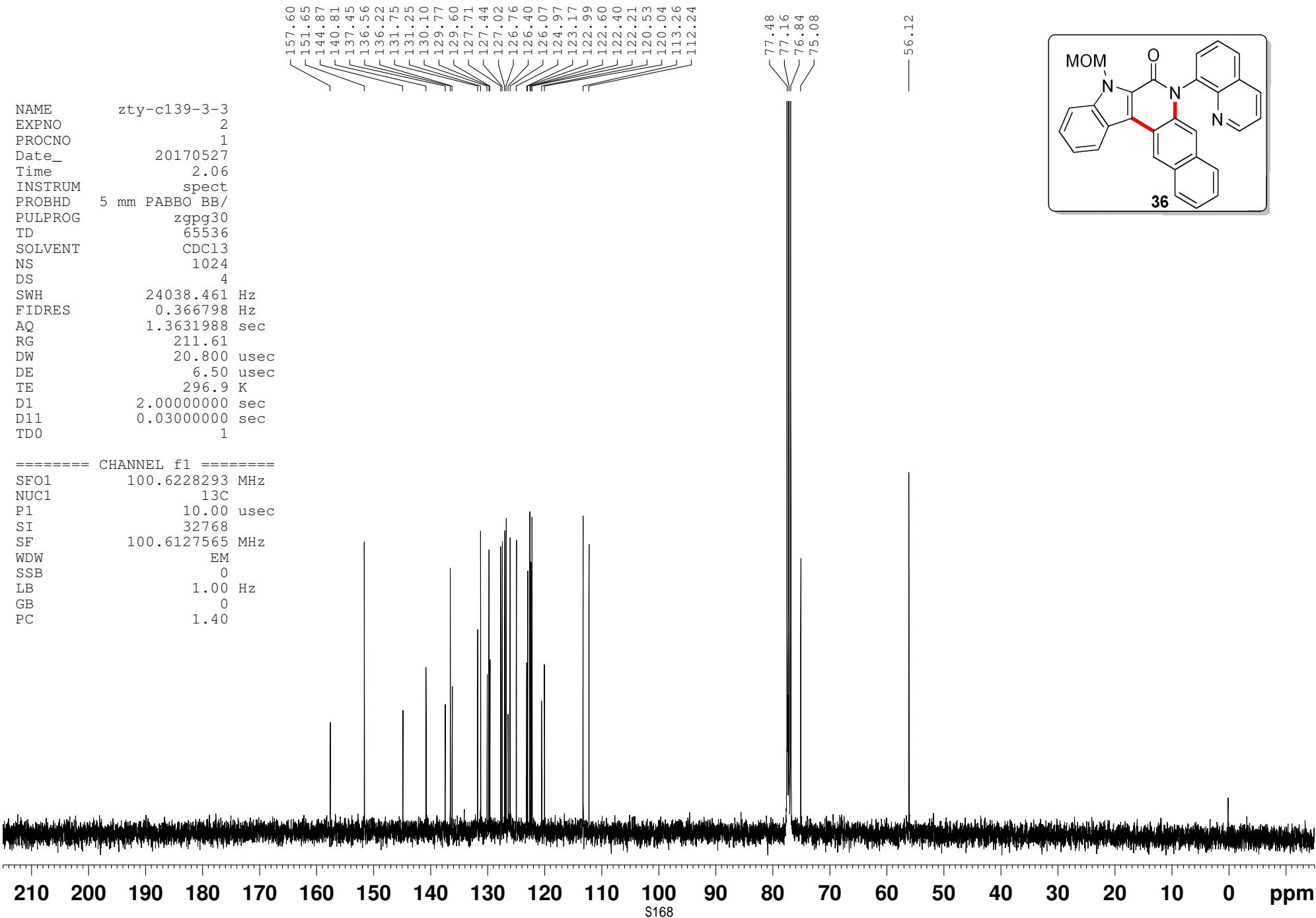


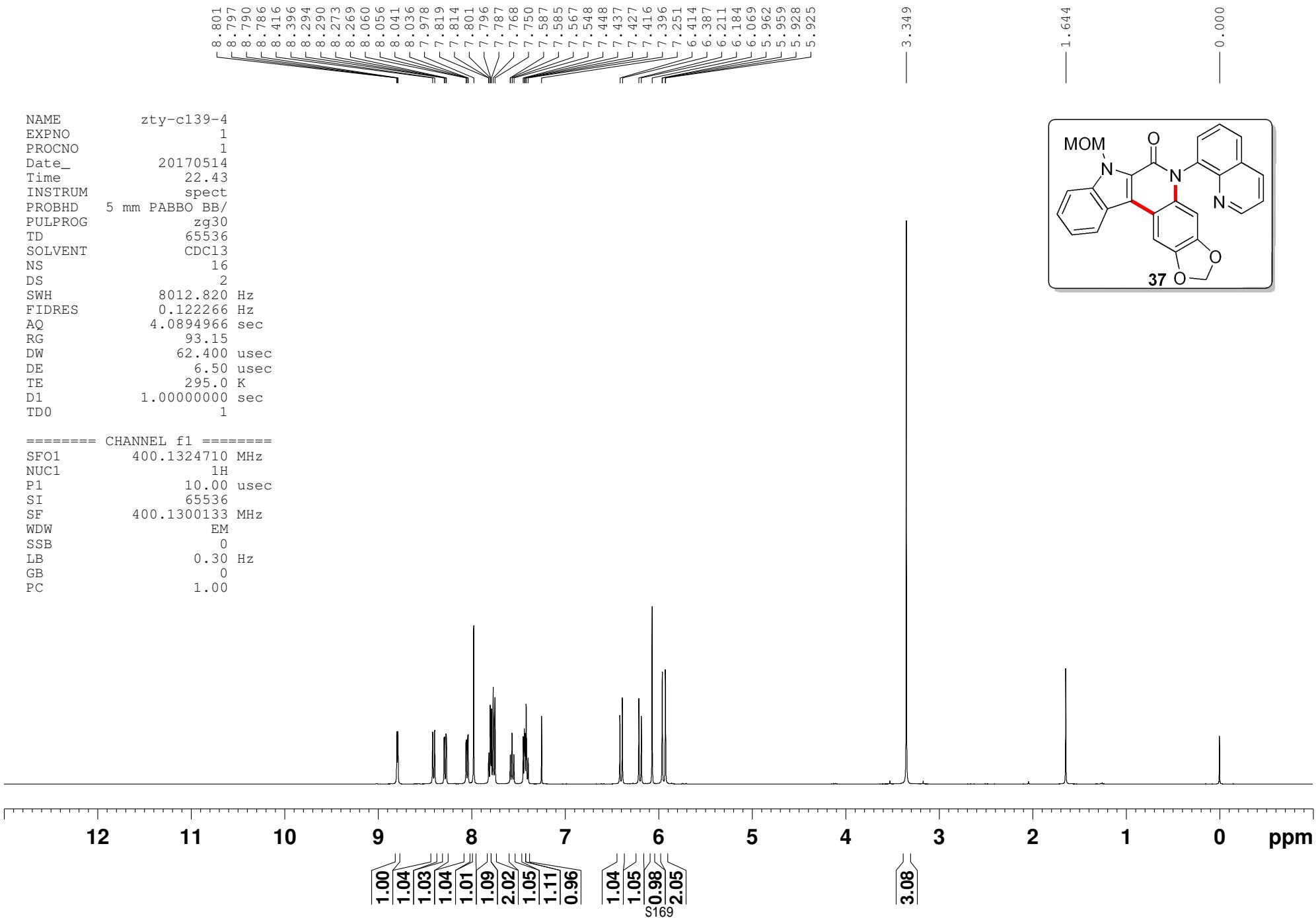
NAME zty-c146-1
 EXPNO 2
 PROCNO 1
 Date_ 20170523
 Time 20.00
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 256
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631988 sec
 RG 211.61
 DW 20.800 usec
 DE 6.50 usec
 TE 297.1 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TDO 1

===== CHANNEL f1 =====
 SFO1 100.6228293 MHz
 NUC1 13C
 P1 10.00 usec
 SI 32768
 SF 100.6127590 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40



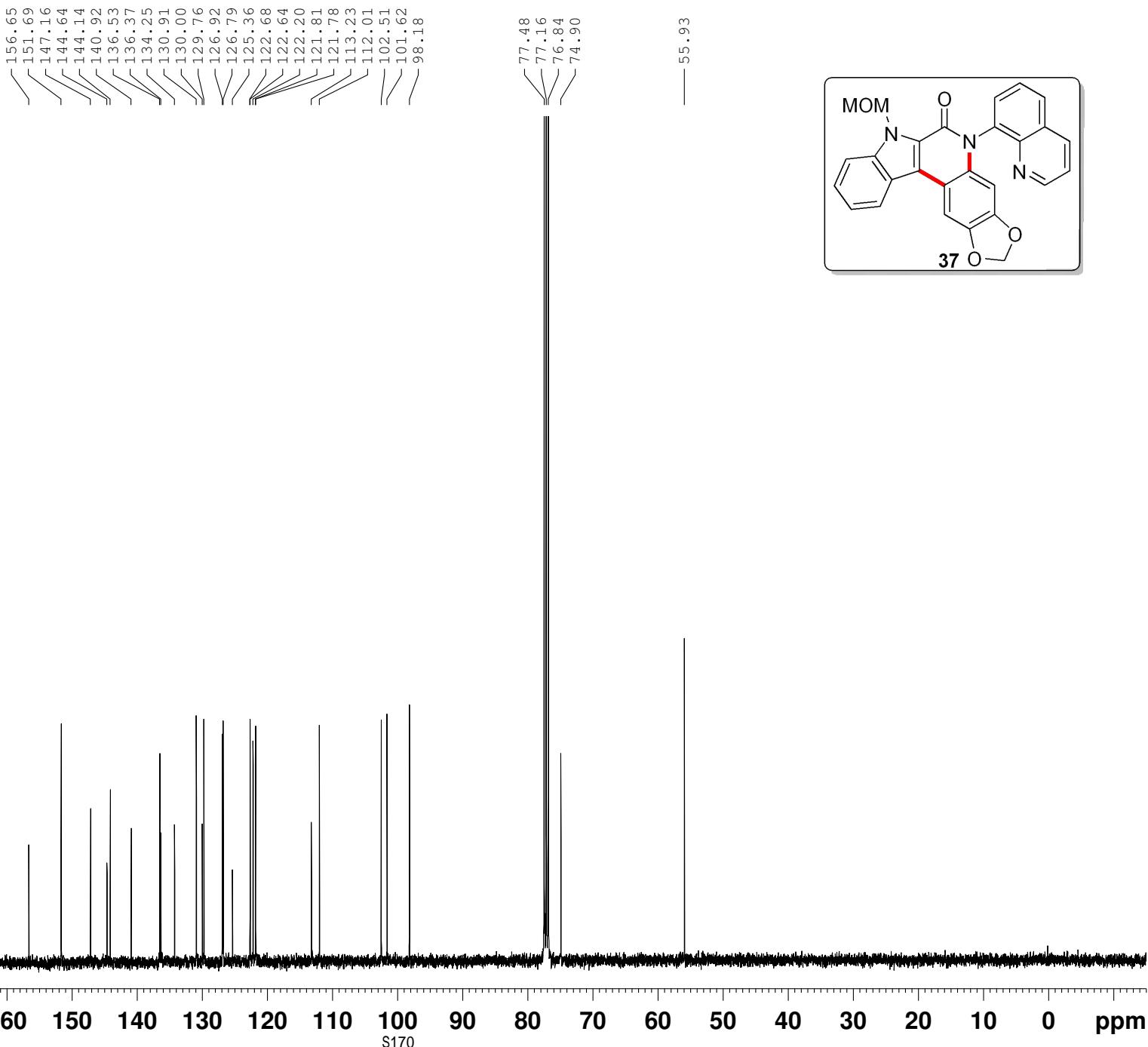


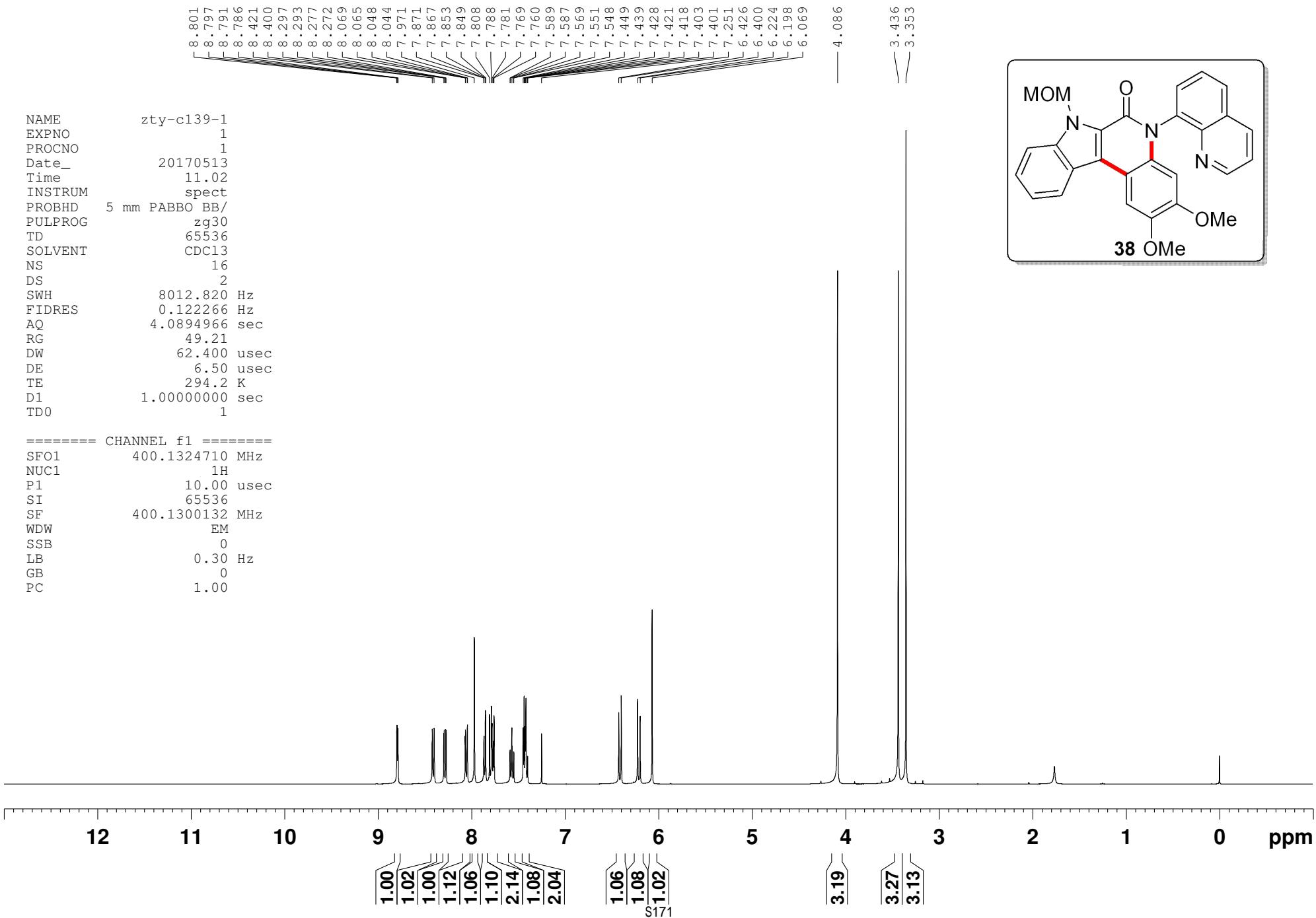




NAME zty-c139-4
 EXPNO 2
 PROCNO 1
 Date_ 20170514
 Time 23.13
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 500
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631988 sec
 RG 211.61
 DW 20.800 usec
 DE 6.50 usec
 TE 295.8 K
 D1 2.0000000 sec
 D11 0.03000000 sec
 TDO 1

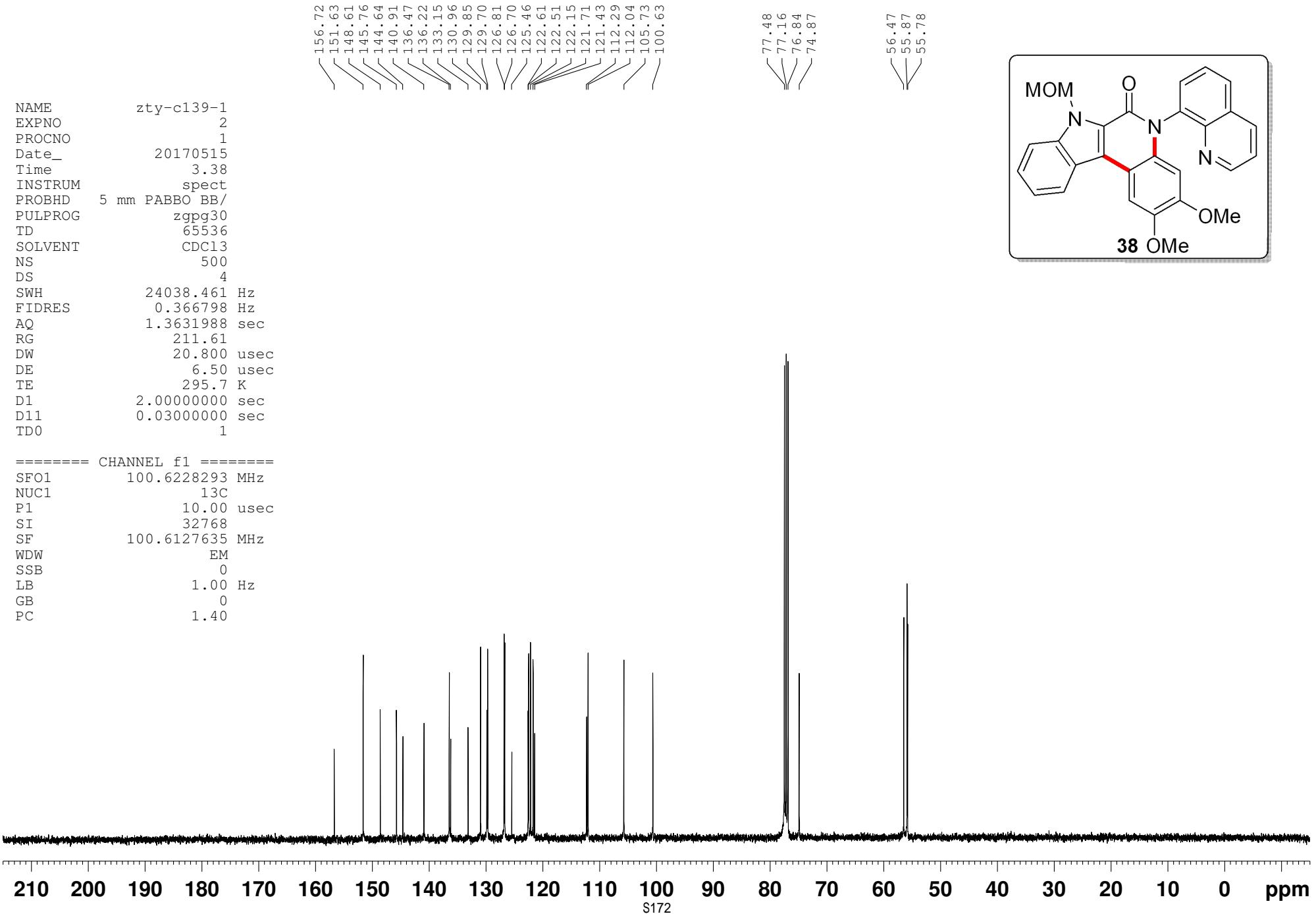
===== CHANNEL f1 =====
 SFO1 100.6228293 MHz
 NUC1 13C
 P1 10.00 usec
 SI 32768
 SF 100.6127589 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

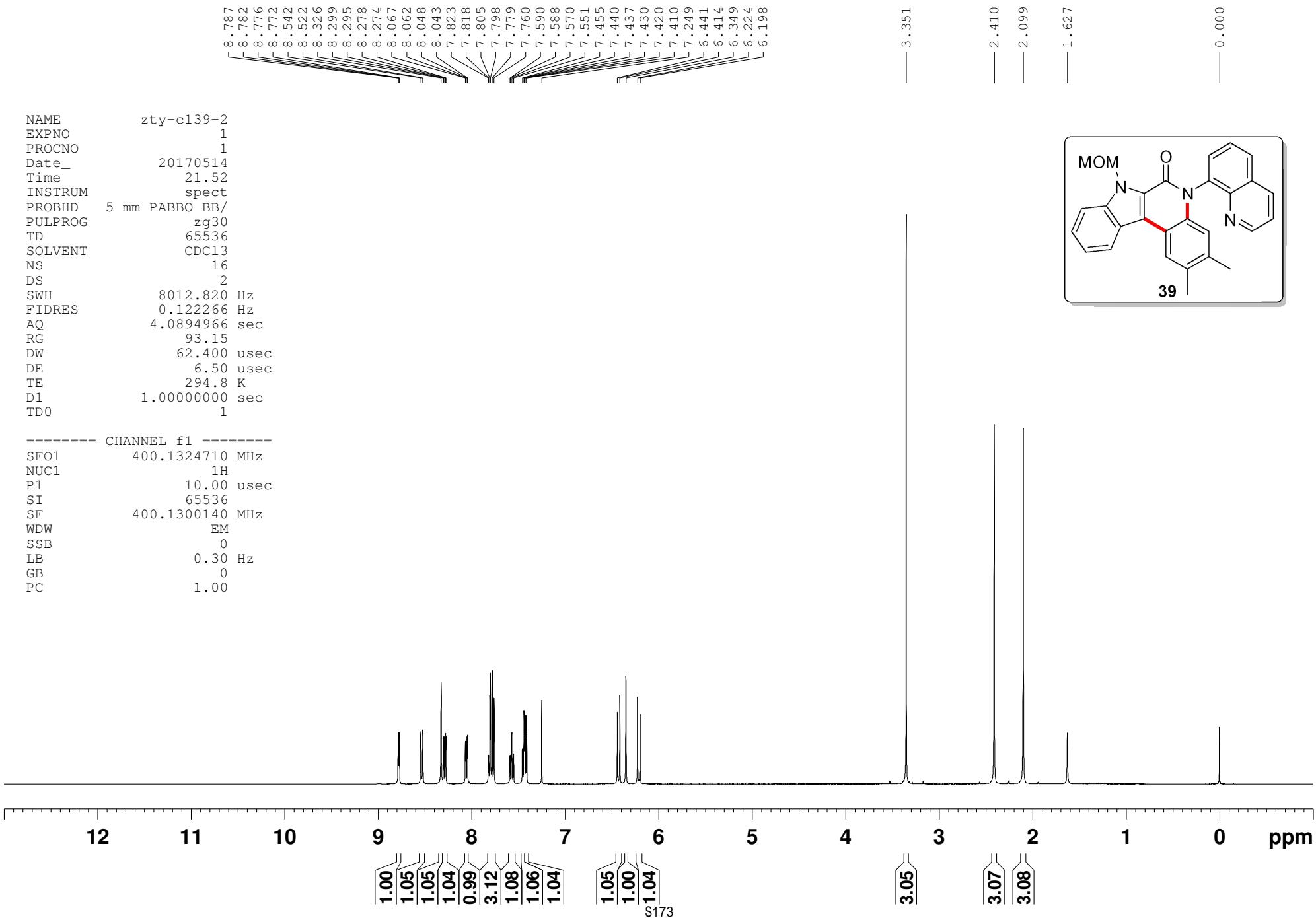




NAME zty-c139-1
 EXPNO 2
 PROCNO 1
 Date_ 20170515
 Time 3.38
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 500
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631988 sec
 RG 211.61
 DW 20.800 usec
 DE 6.50 usec
 TE 295.7 K
 D1 2.0000000 sec
 D11 0.0300000 sec
 TD0 1

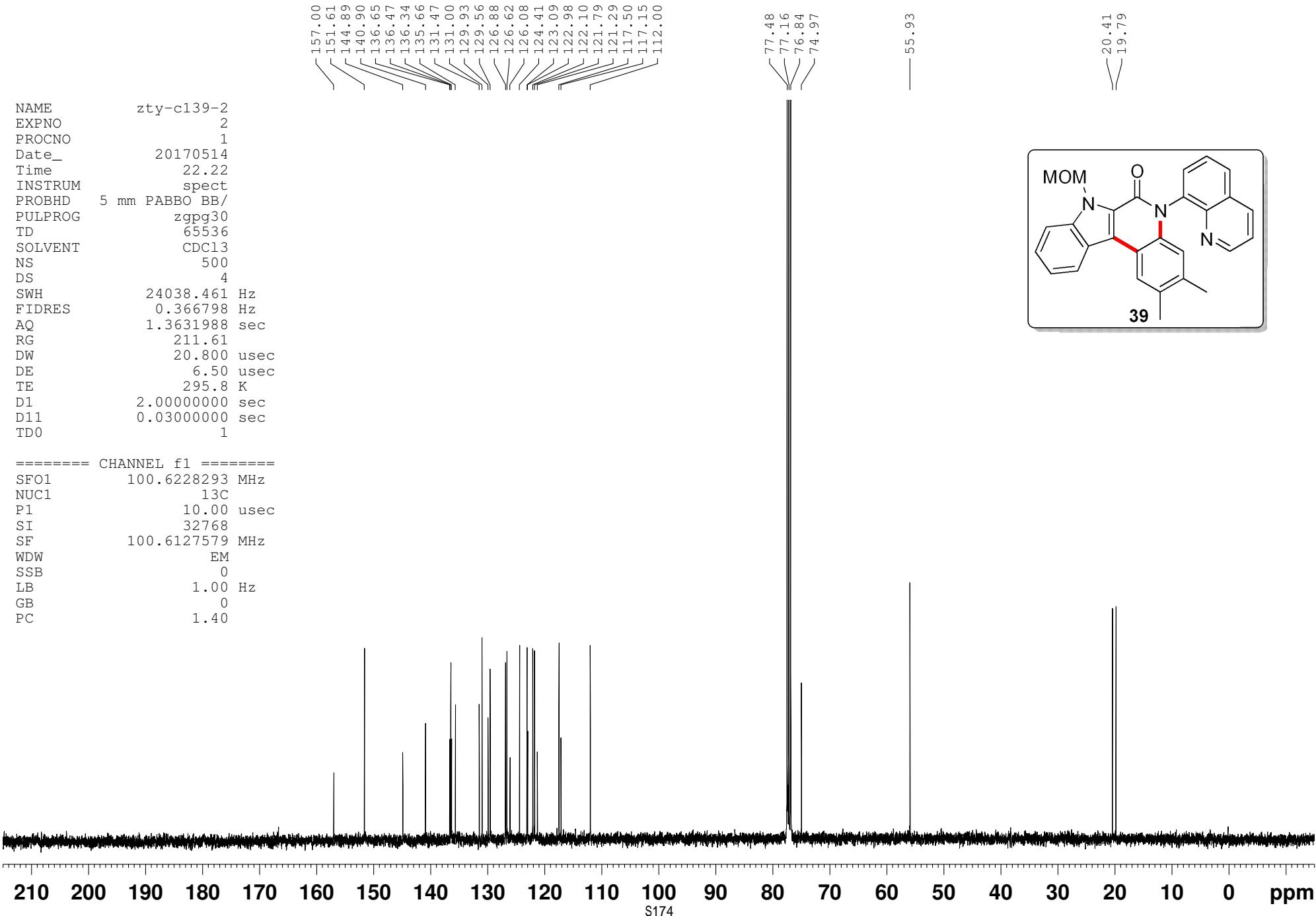
===== CHANNEL f1 =====
 SFO1 100.6228293 MHz
 NUC1 13C
 P1 10.00 usec
 SI 32768
 SF 100.6127635 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

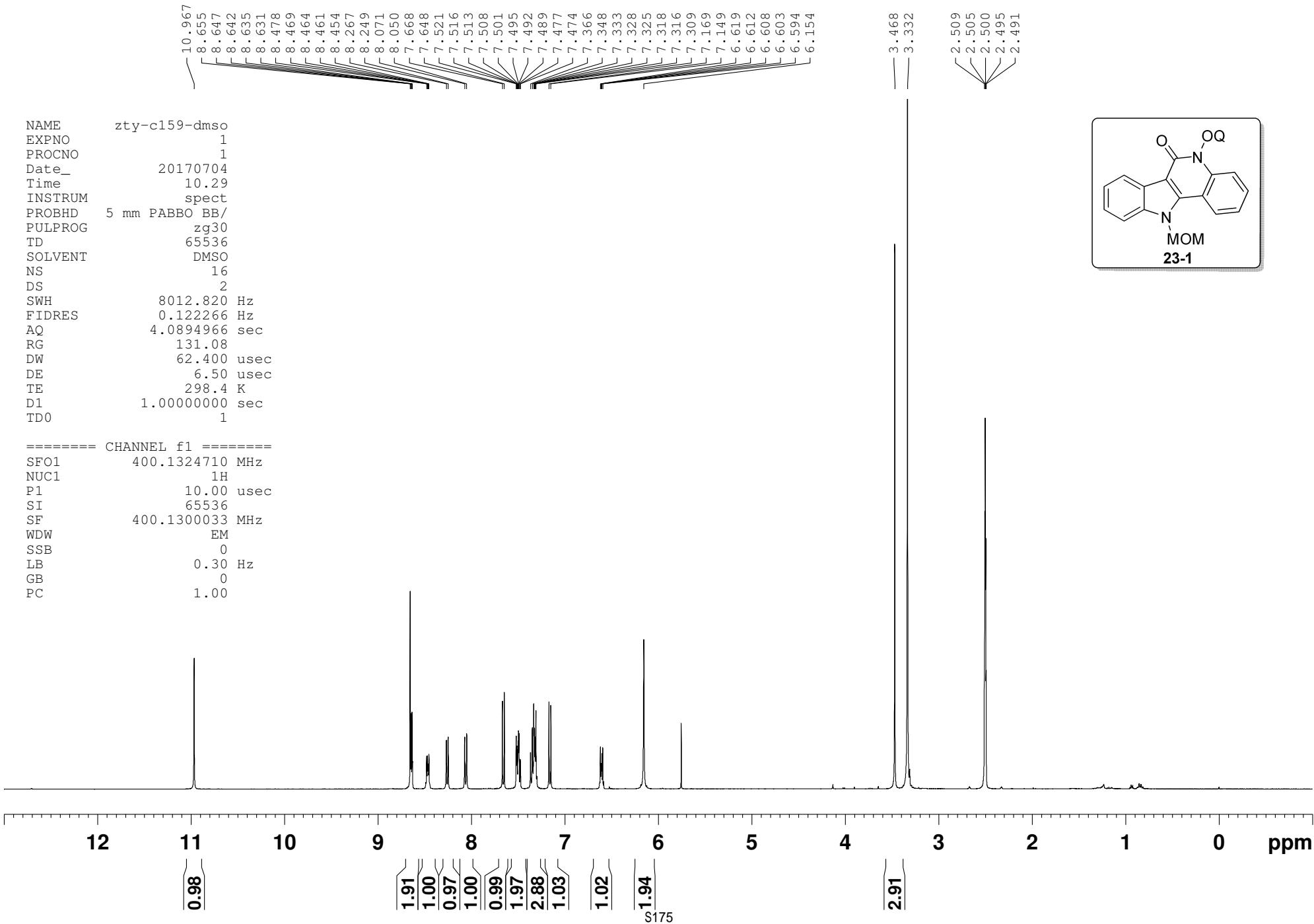




NAME zty-c139-2
 EXPNO 2
 PROCNO 1
 Date_ 20170514
 Time 22.22
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 500
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631988 sec
 RG 211.61
 DW 20.800 usec
 DE 6.50 usec
 TE 295.8 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TDO 1

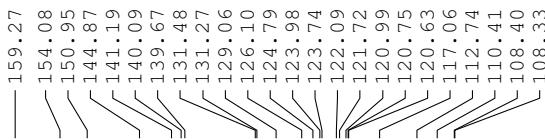
===== CHANNEL f1 =====
 SFO1 100.6228293 MHz
 NUC1 13C
 P1 10.00 usec
 SI 32768
 SF 100.6127579 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40





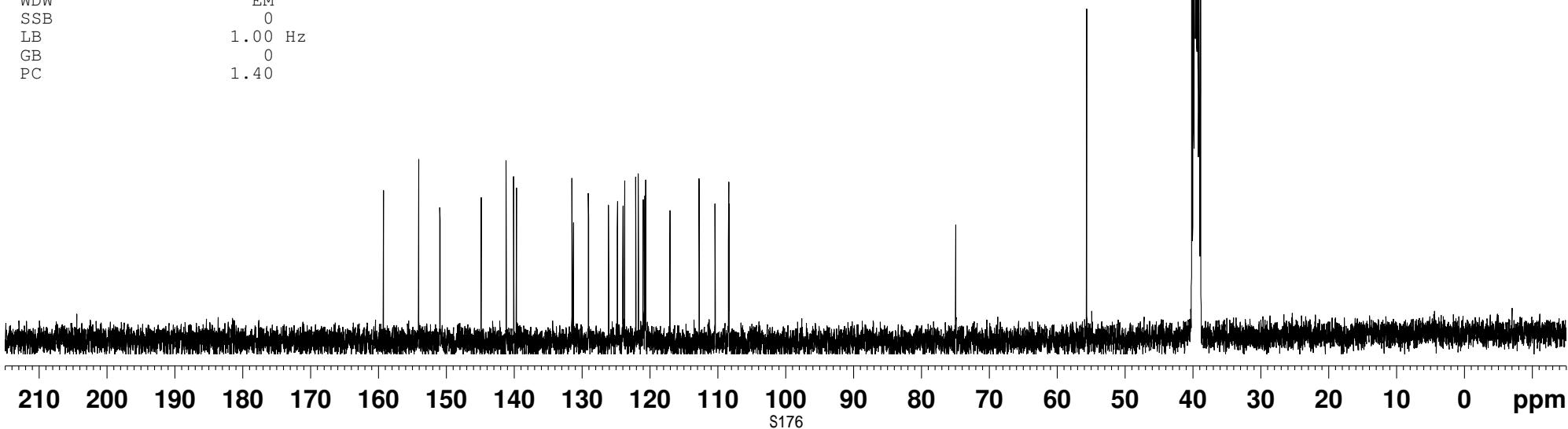
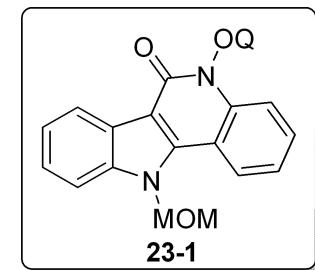
NAME zty-c159-c
 EXPNO 1
 PROCNO 1
 Date_ 20170707
 Time 1.22
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT DMSO
 NS 2000
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631988 sec
 RG 211.61
 DW 20.800 usec
 DE 6.50 usec
 TE 298.9 K
 D1 2.0000000 sec
 D11 0.0300000 sec
 TDO 1

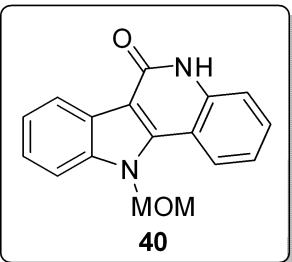
===== CHANNEL f1 =====
 SFO1 100.6228293 MHz
 NUC1 13C
 P1 10.00 usec
 SI 32768
 SF 100.6128188 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40



— 74.93

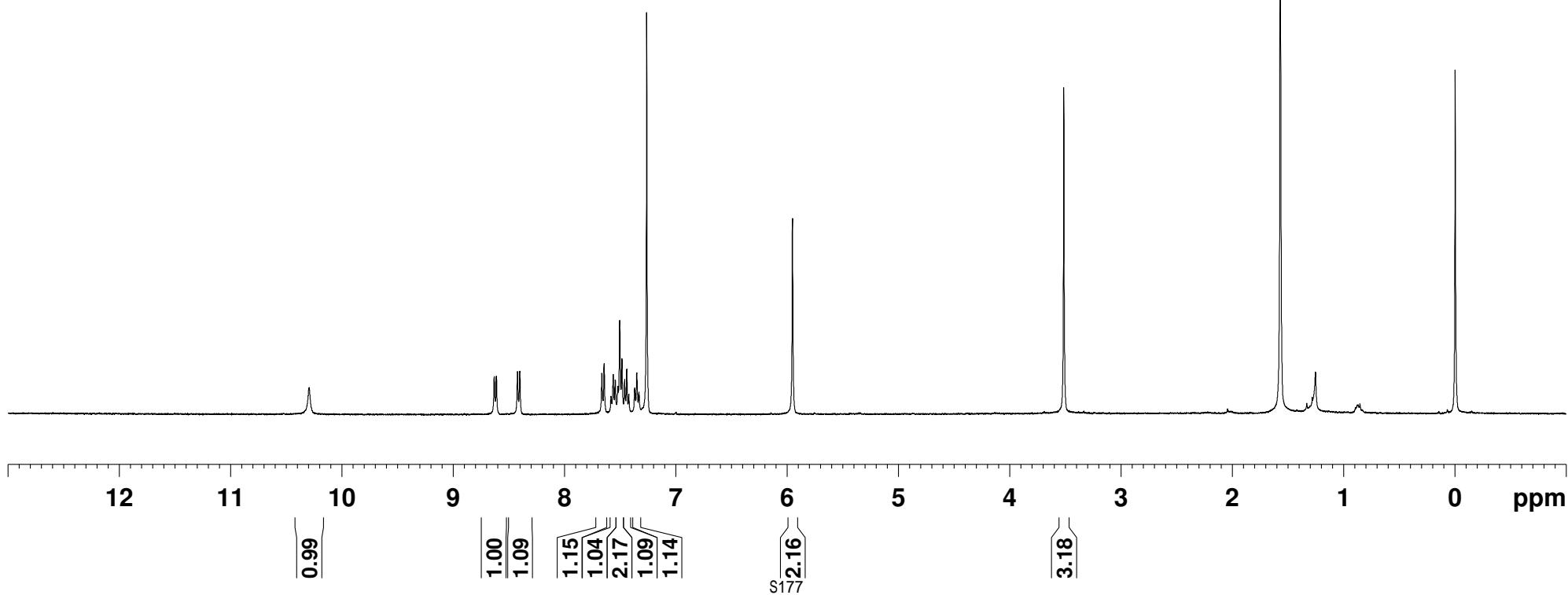
— 55.64

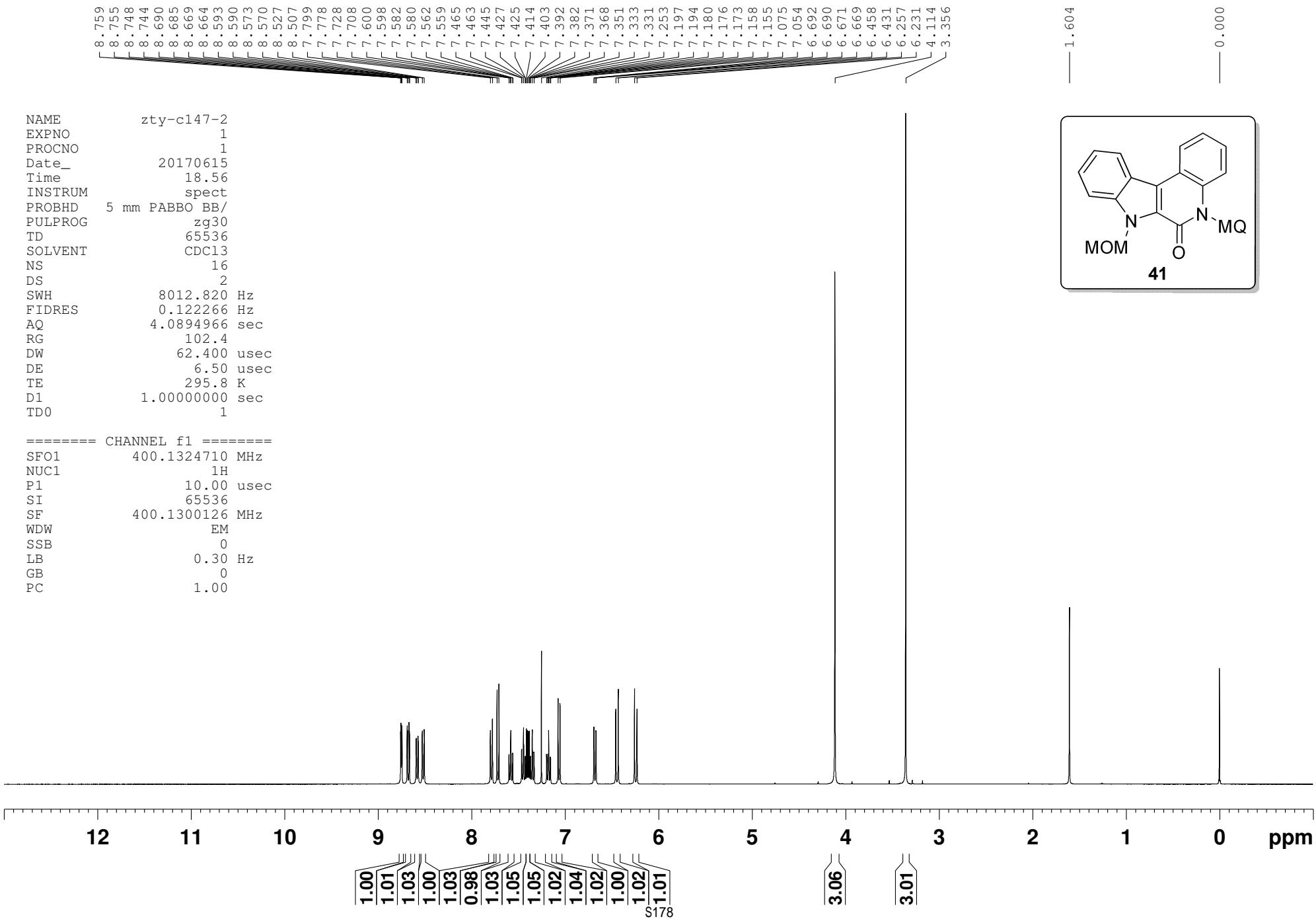




— 10.292

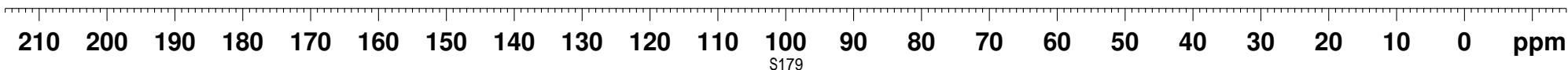
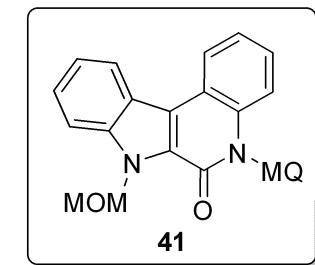
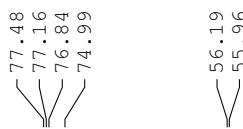
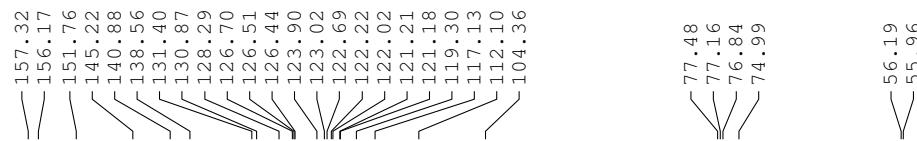
NAME zty-c171-3.fid
EXPNO 1
PROCNO 1

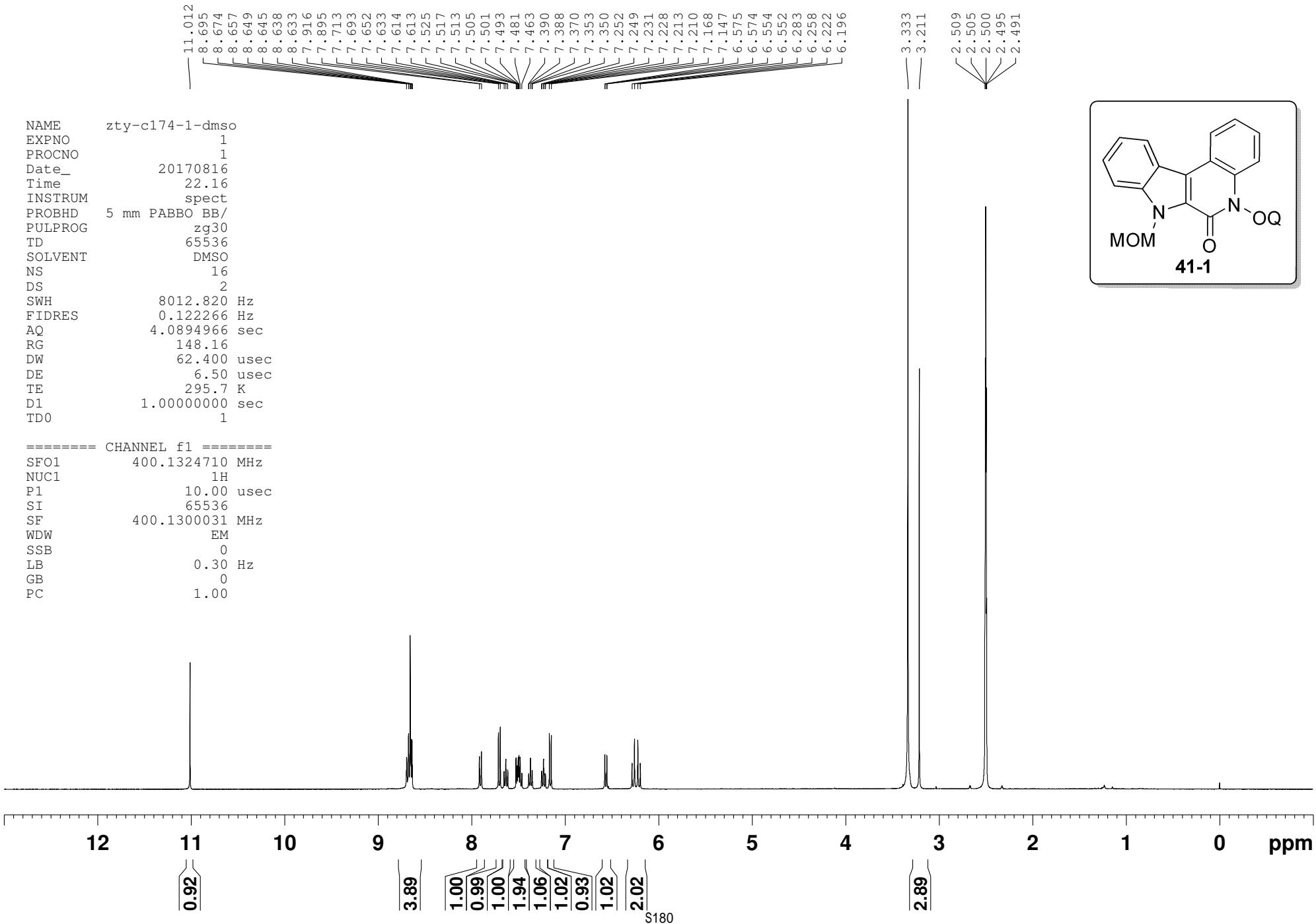




NAME zty-c147-2
 EXPNO 2
 PROCNO 1
 Date_ 20170615
 Time 19.24
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 800
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631988 sec
 RG 211.61
 DW 20.800 usec
 DE 6.50 usec
 TE 296.7 K
 D1 2.0000000 sec
 D11 0.0300000 sec
 TDO 1

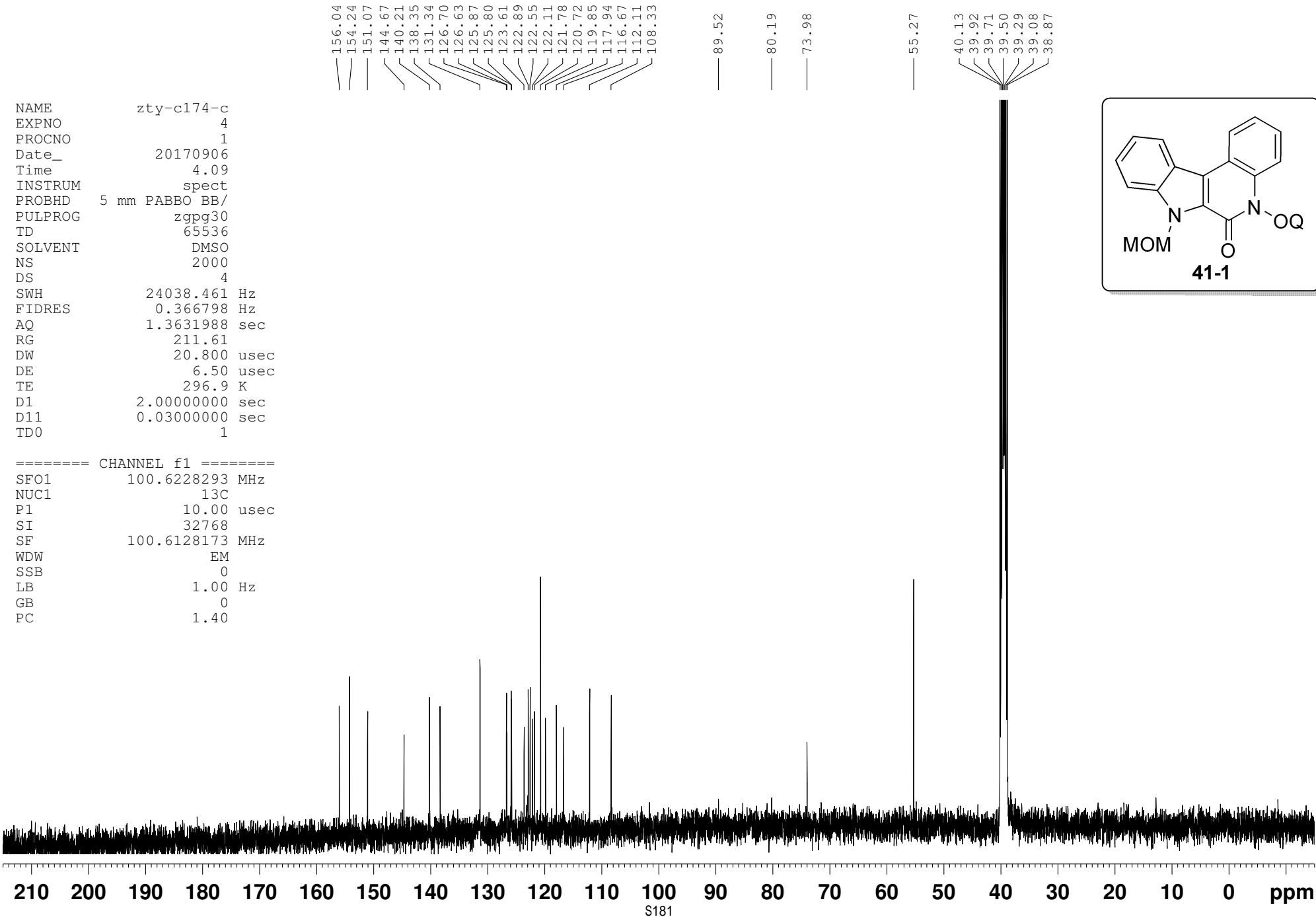
===== CHANNEL f1 =====
 SFO1 100.6228293 MHz
 NUC1 13C
 P1 10.00 usec
 SI 32768
 SF 100.6127571 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

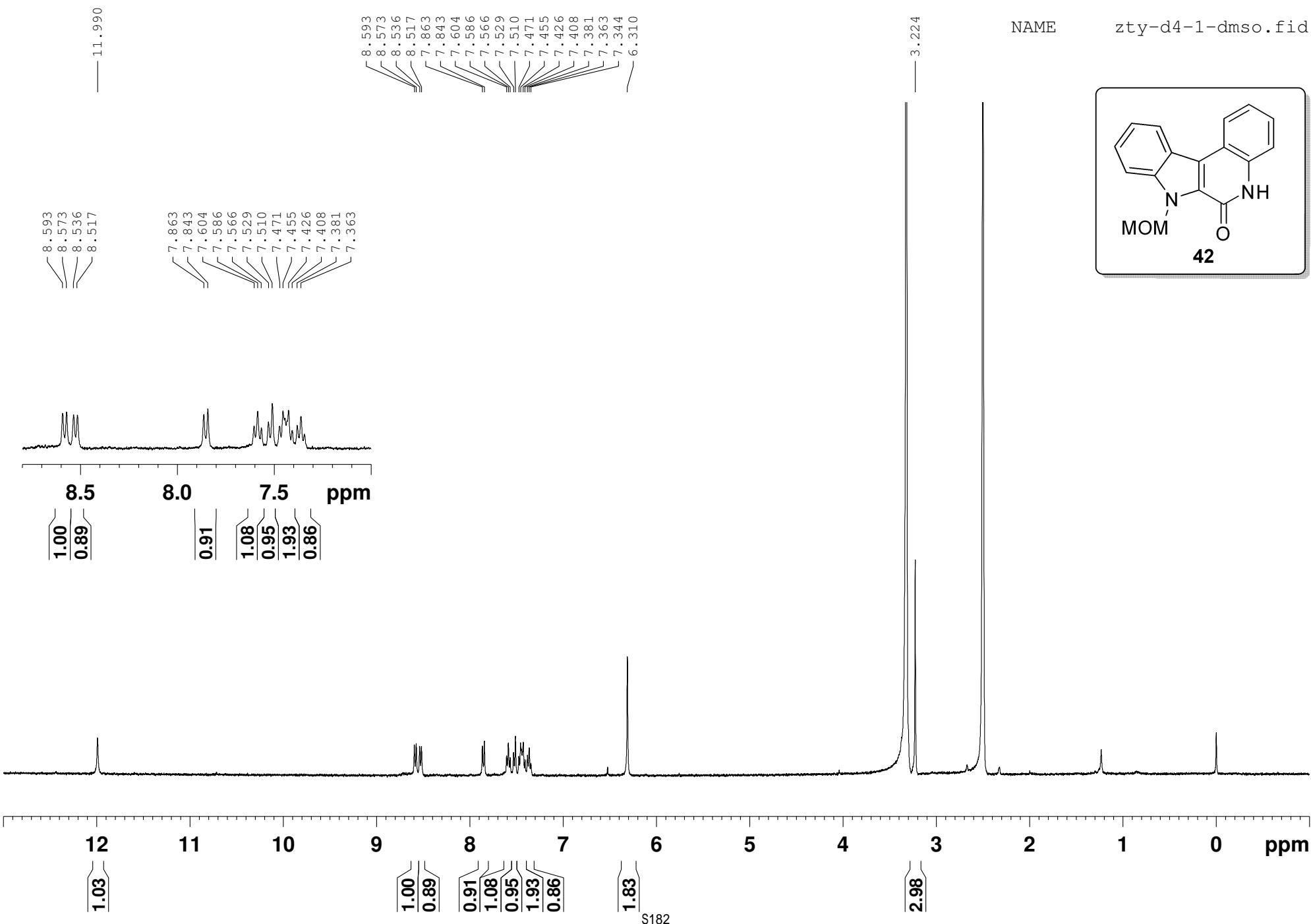


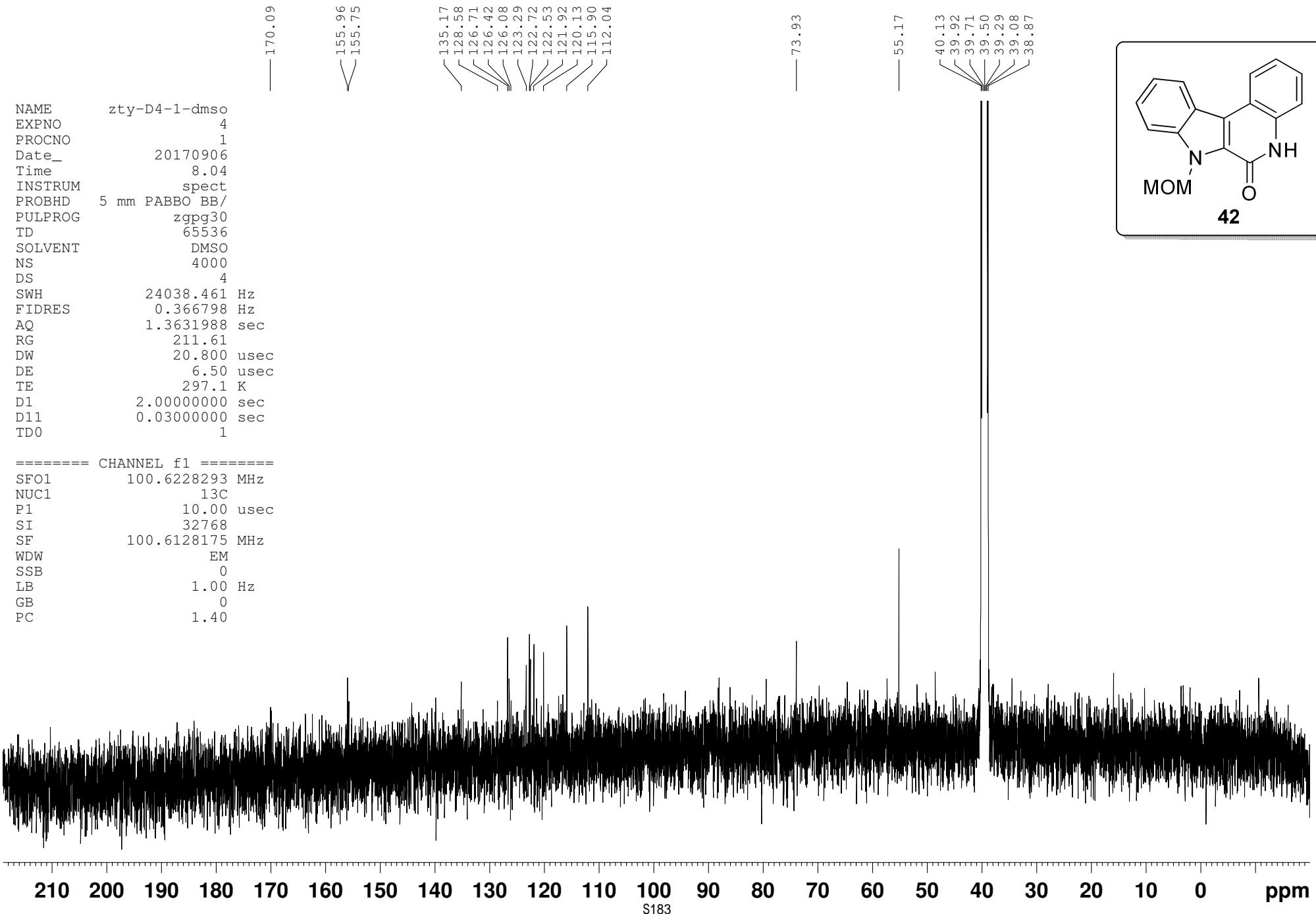


NAME zty-c174-c
 EXPNO 4
 PROCNO 1
 Date_ 20170906
 Time 4.09
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT DMSO
 NS 2000
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631988 sec
 RG 211.61
 DW 20.800 usec
 DE 6.50 usec
 TE 296.9 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TDO 1

===== CHANNEL f1 =====
 SFO1 100.6228293 MHz
 NUC1 13C
 P1 10.00 usec
 SI 32768
 SF 100.6128173 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40







NAME zty-d6-dmso.fid

