Electronic Supplementary Information

Iptycenes with acridinone motif developed through [4 + 2] cycloaddition of tethered naphthalene and iminoquinone via radical reaction

Selvam Raju,[a] Pratheepkumar Annamalai,[a] Pei-Ling Chen,[b] Yi-Hung Liu[c] and Shih-Ching Chuang*[a]

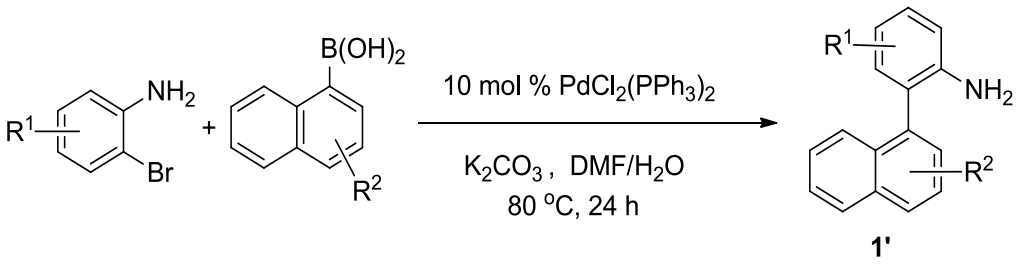
Table of Contents:

General information:

All the reactions were done under air atmosphere. All the obtained products were characterized by melting points (m.p), ^{1}H-NMR, ^{13}C-NMR, mass spectra and infrared spectra (IR). Melting points were measured on an Electrothermal MEL-TEMP melting point apparatus; IR spectra were recorded on a BRUKER spectrometer; ^{1}H-NMR and ^{13}C-NMR spectra were obtained on Aglient-400MHz and chemical shifts were reported in parts per million (ppm, δ) with $CDCl_3$ as a Reference. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), multiplet (m); Coupling constants *J* are quoted in Hz. Carbon-13 nuclear magnetic resonance (^{13}C NMR) data were acquired at 100 MHz. Yields were calculated using mesitylene by NMR. $Cu(OAc)_2.H_2O$, $Pd(PPh_3)_4$, 1,2-dichlorobenzene (ODCB), aromatic amine, aromatic boronic acids, alkenes and other reagents or chemicals were used as purchased without further purification. $PdCl_2(PPh_3)_2$ was prepared from $PdCl_2$ following a literature procedure.[1] Same solvents were used for flash chromatography as eluents used for TLC analysis. During chromatography, we applied pressure by an air pump. Unless otherwise stated, all the reagents were purchased from commercial sources.

A. General procedure for the synthesis of 2-(naphthalen-1-yl)anilines:

The following 2-(naphthalen-1-yl)anilines substrates were prepared by Suzuki-Miyaura coupling reactions between arylbromide and corresponding arylboronic acid.[2]



1'

A 50 mL round bottom flask with a stir bar is fitted with a rubber septum and flame dried under high vacuum. The flask is purged with argon and charged with $PdCl_2(PPh_3)_2$ (10 mol %), K_2CO_3 (10.8 mmol), 2-bromoanilines (2.70 mmol), arylboronic acids (3.20 mmol) and DMF/deoxygenated water (13 mL/3 mL) was added. The reaction mixture was stirred at 80 °C for 24 h under nitrogen atmosphere. After the reaction was cooled down to room temperature, the organic layer was separated and the aqueous layer was extracted with ethyl acetate (10 mL × 3), and the combined organic layer was dried over $MgSO_4$ and concentrated. The crude product was purified by flash chromatography on silica gel to afford 2-(naphthalen-1-yl)anilines.

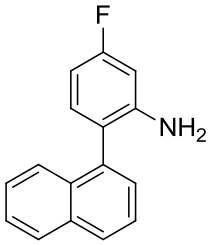
---

[1] Youn, S. W.; Bihn, J. H. *Tetrahedron Lett.* **2009**, *50*, 4598–4601.

[2] Rajeshkumar, V.; Chan, F.-W.; Chuang, S.-C. *Adv. Synth. Catal.* **2012**, *354*, 2473-2483.

B. Spectroscopic and physical data of all new compounds

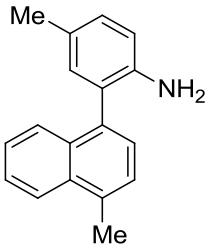
5-fluoro-2-(naphthalen-1-yl)aniline (1a)



Yield 91% (582 mg), pale yellow liquid; R_f = 0.44 (hexanes/EA = 9 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.07 (q, *J* = 8.0, 5.2 Hz, 2H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.68–7.59 (m, 2H), 7.57–7.54 (m, 2H), 7.25–7.20 (m, 1H), 7.42 (td, *J* = 5.8, 2.7 Hz, 1H), 6.60 (dd, *J* = 8.4, 2.4 Hz, 1H), 3.61 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 162.0, 145.9 (d, $^3J_{FC}$ = 11.0 Hz), 135.8, 133.6, 132.2 (d, $^3J_{FC}$ = 9.9 Hz), 131.6, 128.2 (d, $^2J_{FC}$ = 23.5 Hz), 127.7, 126.2 (d, $^2J_{FC}$ = 26.2 Hz), 125.9, 125.7, 121.4 (d, $^4J_{FC}$ = 2.6 Hz), 104.6, 104.4 (d, $^1J_{FC}$ = 303.2 Hz), 101.4 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 3463, 3375, 3050, 2853, 1936, 1590, 1390, 1018; HRMS (ESI$^+$), calcd for $C_{16}H_{12}FN$ (M^+) 238.1027 found 238.1035.

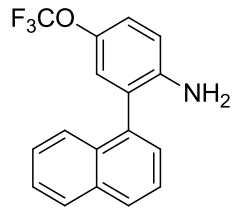
[Note: due to complex splitting, couplings could not be assigned clearly]

4-methyl-2-(4-methylnaphthalen-1-yl)aniline (1b)



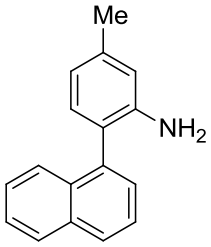
Yield 89% (594 mg), brown liquid; R_f = 0.41 (hexanes/EA = 9 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.26 (d, *J* = 8.0, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.74–7.69 (m, 1H), 7.64–7.61 (m, 1H), 7.59–7.52 (m, 2H), 7.29–7.21 (m, 2H), 6.88 (d, *J* = 8.0 Hz, 1H), 3.51 (s, 2H), 2.95 (s, 3H), 2.55 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 135.1, 133.6, 132.5, 131.4, 131.3, 128.8, 126.9, 126.8, 126.3, 126.2, 125.9, 125.5, 124.4, 124.0, 115.1, 20.1, 19.1 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 3463, 3374, 3201, 3065, 2857, 1875, 1602, 1503, 1421, 1259;HRMS (ESI$^+$), calcd for $C_{18}H_{17}N$ (M^+) 248.1434 found 228.1441.

2-(naphthalen-1-yl)-4-(trifluoromethoxy)aniline (1c)[2]



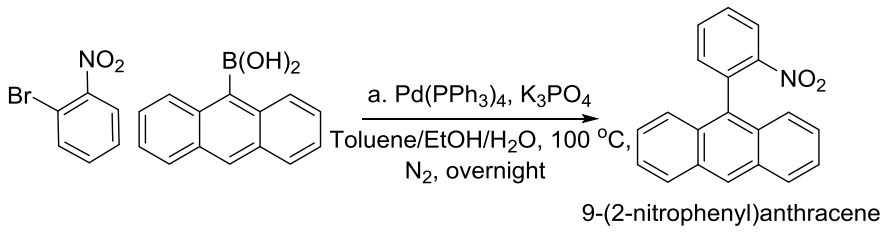
Yield 85% (695 mg), Colorless oil; R_f = 0.39 (hexanes/ethyl acetate = 4:1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.99–7.96 (m, 2H), 7.76–7.71 (m, 1H), 7.63–7.57 (m, 2H), 7.56–7.50 (m, 2H), 7.25–7.17 (m, 2H), 6.80 (d, *J* = 8.4 Hz, 1H), 3.49 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 143.2, 140.9, 135.5, 133.9, 131.3, 128.5, 127.6, 126.5, 126.1, 125.7, 125.6, 124.7 (q, $^1J_{FC}$ = 255.7 Hz), 124.1, 122.1, 121.6. 115.6 ppm.

5-methyl-2-(naphthalen-1-yl)aniline (1d)



Yield 80% (503 mg), yellow solid, m.p. 68−70 °C; R_f = 0.40 (hexanes/EA = 9 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.96 (dd, *J* = 8.4, 6.0 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.61–7.45 (m, 4H), 7.13 (dd, *J* = 6.0, 1.6 Hz, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 6.70 (s, 1H), 3.33 (s, 2H), 2.43 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 138.5, 137.0, 133.8, 131.8, 131.0, 128.2, 127.81, 127.8, 126.1, 126.1, 125.9, 125.8, 123.1, 119.2, 116.0, 21.3 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 3468, 3054, 2857, 1933, 1880, 1617, 1505, 1258; HRMS (ESI^+), calcd for $C_{17}H_{15}N$ (M^+) 234.1277 found 234.1285.

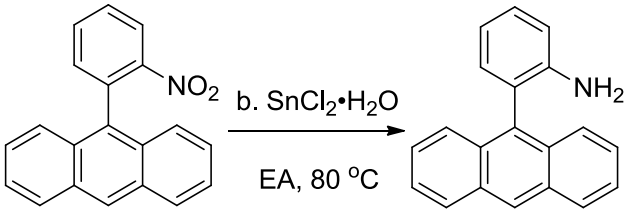
C. Synthesis of 2-(anthracen-9-yl)aniline (1e)[3]



a. A 50 mL round bottom flask with a stir bar is fitted with a rubber septum and flame dried under high vacuum. The flask was purged with argon and charged with 2-bromonitrobenzene (530 mg, 2.64 mmol), 9-anthraceneboronic acid (500 mg, 2.3 mmol), K_3PO_4 (1.6 g, 7.8 mmol) and solvent (toluene/EtOH/H_2O, 3:3:2, 22 mL) and degassed with N_2 for 15 min. Then $Pd(PPh_3)_4$ (57 mg, 0.05 mmol) was added. The

[3] Gao, Y.-X.; Huang, Y. *Adv. Synth. Catal*. **2010**, 352, 1955 – 1966.

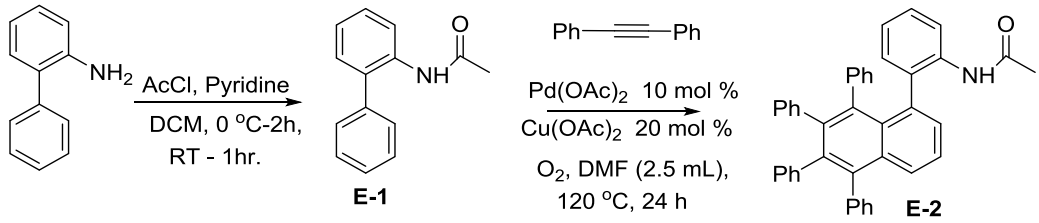
resulting mixture was heated to 100 °C and refluxed under N_2 overnight. Then the reaction mixture was cooled to room temperature and extracted with EtOAc (40 mL × 3). Combined organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography furnishing 585 mg (87%) compound 9-(2-nitrophenyl)anthracene as a yellow solid.



9-(2-nitrophenyl)anthracene **1e**

b. A 50 mL round bottom flask with a stir bar is fitted with a rubber septum and flame dried under high vacuum. The flask was purged with argon and charged with compound 9-(2-nitrophenyl)anthracene (490 g, 1.64 mmol) in 10 mL EtOAc and was added $SnCl_2 \cdot 2H_2O$ (1.7 g, 8.2 mmol) under stirring. The reaction mixture was refluxed at 80 °C overnight before cooled to room temperature. Then the mixture was made slightly alkaline by careful addition of saturated aqueous $NaHCO_3$ solution. The formed slurry was filtered and two layers of the filtrate were separated. Aqueous phase was extracted with EtOAc for three times (50 mL × 3). The combined organic phase was dried over anhydrous Na_2SO_4, concentrated and purified by flash chromatography to give 361 mg (82%) product of 2-(anthracen-9-yl)aniline as a white solid **(1e)**. Yield 80% (353 mg), R_f = 0.3 (hexanes/EtOAc = 40/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.08 (d, *J* = 8.5 Hz, 2H), 7.74 (d, *J* = 8.8 Hz, 2H), 7.51–7.48 (m, 2H), 7.43–7.37 (m, 3H), 7.20 (dd, *J* = 7.5 Hz, 1.3 Hz, 1H), 7.00 (td, *J* = 7.4 Hz, 0.95 Hz, 1H), 6.95 (dd, *J* = 8.1 Hz, 0.55 Hz, 1H), 3.33 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.0, 133.3, 132.1, 131.7, 130.4, 129.0, 128.5, 127.0, 126.5, 125.8, 125.3, 123.5, 118.5, 115.5.

D. Synthesis of *N*-(2-(5,6,7,8-tetraphenylnaphthalen-1- yl)phenyl)acetamide[4]

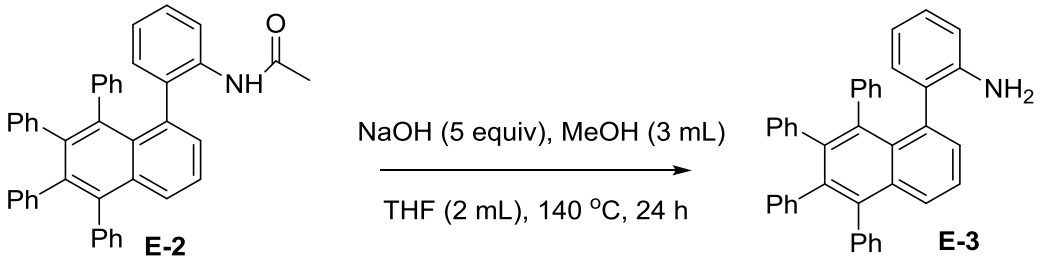


Biphenyl-2-amines (10 mmol) in CH_2Cl_2 (50 mL) was added pyridine (11 mmol) and acetyl chloride (11 mmol) at 0 °C under nitrogen atmosphere. The reaction mixture was warmed to room temperature and stirred until completion of the reaction. The solvent was removed under vacuum. The residue was diluted with H_2O (15 mL), and then extracted with EtOAc (20 mL×3).

[4] Annamalai, P.; Chuang, S.-C. *Adv. Synth. Catal.* **2016**, 358, 1–8.

The combined organic layers were washed with brine (40 mL), dried over anhydrous sodium sulfate and concentrated. The residue was purified by column chromatography on silica gel with ethyl acetate and hexanes as eluents to afford *N*-(biphenyl-2-yl) acetamides (**E-1**). Further, to a 15 mL dried reaction tube, NaOAc (0.25 mmol), *N*-Acyl-2-aminobiaryls **E-1** (0.5 mmol), $Pd(OAc)_2$ (0.05 mmol), diphenyl acetylene (1.2 mmol), $Cu(OAc)_2$ (0.1 mmol) and a stir bar were added. Then, freshly distilled DMF (2.5 mL) was added, and the tube was purged with O_2 for 15 min. Then the tube was placed in an oil bath at 120 °C with vigorous stirring for 24 h. Upon completion of the reaction, the reaction mixture was cooled to room temperature and diluted with ethyl acetate followed by filtration through a thin pad of celite. The filtrate was concentrated by vacuum and crude residue was purified by silica gel column chromatography (hexanes/EtOAc) to afford N-(2-(5,6,7,8-tetraphenylnaphthalen-1-yl)phenyl) acetamides **E-2**. Off-white solid; Yield: 60% (170 mg).

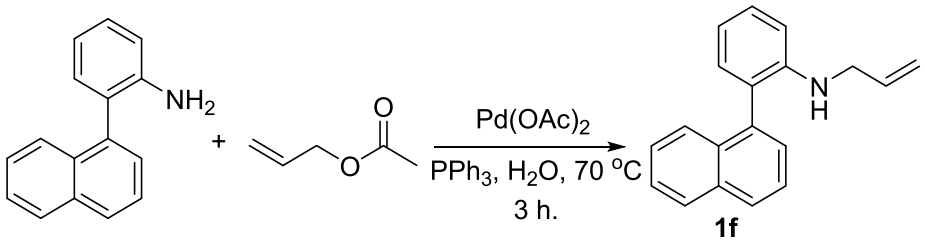
E. Synthesis of 2-(5,6,7,8-tetraphenylnaphthalen-1-yl)aniline (E-3)



To a 15 mL dried reaction tube compound **E-2** (0.5 mmol, 0.28 g), NaOH (3 mmol, 120 mg) and equipped with stirring bar. Then MeOH:THF (2:0.5, 5 mL) was injected into reaction mixture. After the reaction tube was closed with a Teflon cap. Then reaction mixture was heated for 24 h at 140 °C with stirring. Upon cooling down to room temperature, the reaction mixture was neutralized with (10 mL X 3) of 1N HCl and followed by work up with $NaHCO_3$. Further, the organic layer was dried over Na_2SO_4 and the filtrate was concentrated in vacuum, then the residue was purified by flash chromatography (eluent: hexane: ethyl acteate = 9:1) to afford product **E-3.** Off-white solid; Yield: 67% (173 mg), m.p. 148−150 °C; R_f = 0.27 (hexanes/EtOAc = 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.8 Hz, 1H), 7.44 (t, *J* = 7.8, Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.27−7.17 (m, 4H), 6.99−6.98 (m, 1H), 6.83−6.65 (m, 17H), 6.46 (t, *J* = 7.4 Hz, 1H) , 6.19 (d, *J* = 8.0 Hz, 1H), 3.12 (s, 2H) ppm; ^{13}C NMR (100 MHz, CDCl3) δ142.7, 141.0, 140.6, 140.6, 140.0, 139.9, 139.0, 138.8, 138.3, 137.5, 133.6, 132.5, 131.4, 131.3, 131.3, 131.2, 131.2, 131.1, 131.0, 130.4, 130.0, 129.5, 127.52, 127.50, 127.45, 127.3, 126.44, 126.41, 126.12, 126.10, 125.8, 125.7, 125.41, 125.40, 125.2, 124.9, 117.6, 115.0 ppm; FT-IR (KBr) ṽ (cm−1) 3471, 3382, 3056, 2853, 1576, 1140, 1001; HRMS (ESI$^+$): calcd for $C_{40}H_{29}N$ (M^+) 524.2373 found 524.2378.

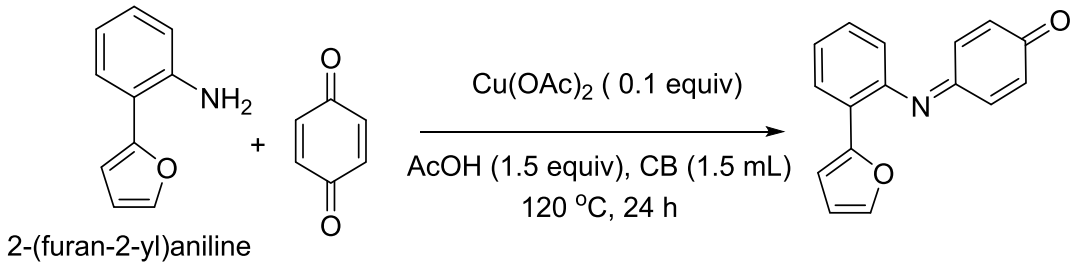
F. Synthesis of N-allyl-2-(naphthalen-1-yl)aniline (1f)[5]

[5] Shih, C.-J.; Shue, Y.-J.; Yang, S.-Y.; Yang, S.-C., *Appl. Organometal. Chem.* **2012,** *26*, 550.



Reaction with 2-(naphthalen-1-yl)aniline : A 10 mL tube boiling tube equipped with a stirring bar was charged with 1-aminonaphthalene (1a) (109.5 mg, 0.5 mmol), allyl acetate (51.6 mg, 0.6 mmol), $Pd(OAc)_2$ (2.24 mg, 0.01 mmol) and PPh_3 (10.5 mg, 0.04 mmol) in water (3 g) was heated to 70 °C for 1h. After the mixture was cooled down to room temperature, water and brine were added. The organic layer were extracted with ether, dried over $MgSO_4$ and concentrated under vacuum. The crude product was purified by column chromatography on silica gel with hexane: ethyl acetate (9.8:0.2) and afforded **1f** (79 mg, 61%), colorless sticky liquid; R_f = 0.63 (hexanes/EtOAc = 44/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97(t, *J* = 8.4 Hz, 2H), 7.74(d, *J* = 8.4 Hz, 1H), 7.63(t, *J* = 7.5 Hz, 1H), 7.57–7.52(m, 2H), 7.49–7.45(m, 1H), 7.41–7.37(m, 1H), 7.22(dd, *J* = 6.0, 1.4 Hz, 1H), 6.92(t, *J* = 7.4 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1 H), 5.85–5.77(m, 1H), 5.18–5.07(m, 2H), 3.75(d, *J* = 4.8 Hz, 2H), 3.66(s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 136.8, 135.3, 133.8, 131.9, 130.9, 128.8, 128.2, 128.0, 127.8, 126.1, 126.1, 126.0, 125.8, 125.7, 116.7, 115.6, 110.5, 46.1 ppm; HRMS (ESI$^+$), calcd for $C_{19}H_{17}N$ (M^+) 260.1438 found 260.1439.

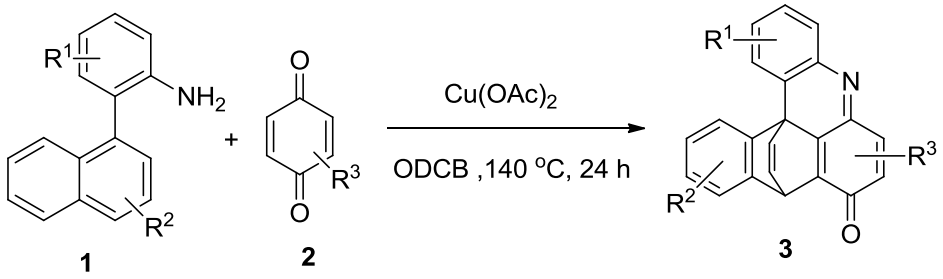
G. Synthesis of 4-((2-(furan-2-yl)phenyl)imino)cyclohexa-2,5-dienone (1g)



A 15 mL tube equipped with a stirring bar was charged with $Cu(OAc)_2$ (0.1 equiv), *p*-benzoquinone (0.45 mmol, 1.5 equiv), and 2-(furan-2-yl)aniline (0.3 mmol) was added in presence of air atmosphere. Then chlorobenzene (1.5 mL) and glacial acetic acid (1.2 equiv) were added via a syringe and the resulting mixture was heated for 24 h at 120 °C with stirring. Upon completion of the reaction, the reaction mixture was worked up through silica gel by passing 50 mL of hexanes. Last, the reaction mixture was concentrated in vacuum and purified by chromatography to afford product (**1g)**. Yield 35% (26 mg), red solid, m.p. 104−106 °C; R_f = 0.41 (hexanes/EA = 9 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.94 (d, *J* = 7.2 Hz, 1H), 7.46–7.41 (m, 2H), 7.30–7.23 (m, 3H), 7.05 (d, *J* = 10.0 Hz, 1H), 6.73 (d, *J* = 10.0 Hz, 1H), 6.63 (d, *J* = 7.2

Hz, 1H), 6.50–6.42 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.3, 157.4, 150.4, 144.9, 142.2, 141.4, 133.4, 133.1, 128.5, 127.1, 126.4, 126.1, 122.6, 119.9, 111.9, 111.2 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 3117, 3059, 2955, 2849, 1726, 1579, 1155; HRMS (ESI^+), calcd for $C_{16}H_{11}NO_2$ (M^+) 250.0863 found 250.0871.

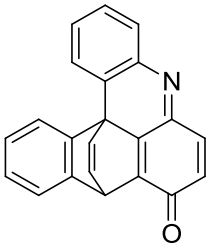
H. General procedure for the synthesis of 9,13*b*-ethenonaphtho[3,2,1-*kl*]acridin-8(9*H*)-one



A 15 mL tube equipped with a stirring bar was charged with $Cu(OAc)_2$ (2 equiv), *p*-benzoquinone (0.17 mmol, 1.7 equiv) and 2-aminobiaryl (0.1 mmol) was added in presence of air atmosphere. Then ODCB (2 mL) and glacial acetic acid(0.18 mmol, 10 µL) were added via syringe and the resulting mixture was heated for 24 h at 140 °C with stirring. Upon completion of the reaction, the reaction mixture was worked up by passing through silica gel with elution of 50 mL of hexane. The reaction mixture was concentrated in vacuum and purified by thin layer chromatography to afford product (**3**). Zero to a few percents of intermediate iminoquinones were observed.

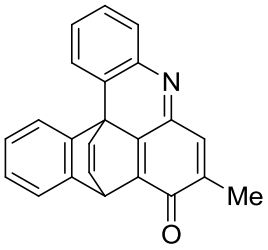
I. Spectroscopic and physical data of all new compounds of 9,13b-ethenonaphtho[3,2,1-kl]acridin-8(9H)-one derivatives.

9,13*b*-ethenonaphtho[3,2,1-*kl*]acridin-8(9*H*)-one (3a)



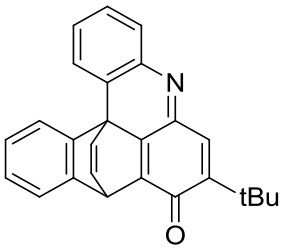
Yield 78% (24 mg), yellow solid, m.p. 216−218 °C; R_f = 0.20 (hexanes/EA = 9 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95–7.93 (m, 1H), 7.73–7.71 (m, 1H), 7.66–7.60 (m, 2H), 7.41 (d, *J* = 7.2, 1H), 7.22 (dd, *J* = 7.6, 2.4 Hz, 1H), 7.04–6.95 (m, 3H), 6.89–6.86 (m, 2H), 6.55 (dd, *J* = 7.6, 2.2 Hz, 1H), 5.80 (dd, *J* = 4.8, 1.2, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.3, 151.9, 148.0, 145.2, 145.1, 144.8, 144.6, 142.1, 137.6, 136.7, 132.9, 132.4, 130.5, 129.9, 129.6, 129.3, 125.0, 124.2, 124.1, 122.1, 55.2, 45.5 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 3259, 3056, 2955, 2928, 1947, 1771, 1719, 1506; HRMS (ESI^+), calcd for $C_{22}H_{13}NO$ (M^+) 308.1069 found 308.1075.

7-methyl-9,13*b*-ethenonaphtho[3,2,1-*kl*]acridin-8(9*H*)-one (3b)



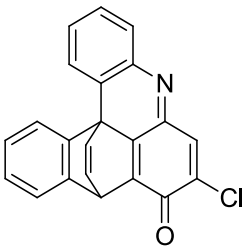
Yield 67% (22 mg), yellow solid, m.p. 194−196 °C; R_f = 0.22 (hexanes/EA = 9 : 1); ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.92–7.90 (m, 1H), 7.72–7.70 (m, 1H), 7.63–7.60 (m, 2H), 7.40 (d, *J* = 7.2 Hz, 1H), 7.04–7.01 (m, 2H), 7.00–6.95 (m, 2H), 6.87 (d, *J* = 4.0, 2H), 5.80 (d, *J* = 4.8 Hz, 1H), 2.09 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.7, 152.1, 148.1, 145.3, 145.1, 144.6 (2C), 142.5, 141.1, 136.9, 133.8, 132.6, 130.0, 129.8, 129.4, 129.2, 124.9, 124.14, 124.06, 122.1, 55.0, 45.7, 16.3 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 3223, 2918, 2949, 1730, 1620, 1565, 1227; HRMS (ESI$^+$), calcd for $C_{23}H_{15}NO$ (M^+) 322.1226 found 322.1229.

7-(*tert*-butyl)-9,13*b*-ethenonaphtho[3,2,1-*kl*]acridin-8(9*H*)-one (3c)



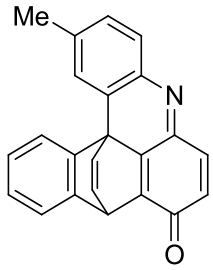
Yield 55% (20 mg), yellow solid, m.p. 188−190 °C; R_f = 0.40 (hexanes/EA = 9 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.93–7.89 (m, 1H), 7.74–7.71 (m, 1H), 7.64–7.59 (m, 2H), 7.43 (d, *J* = 7.2 Hz, 1H), 7.09 (s, 1H), 7.05–6.96 (m, 3H), 6.91–6.86(m, 2H), 5.80 (dd, *J* = 4.4, 1.4 Hz, 1H), 1.32 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.4, 152.4, 151.9, 148.2, 146.3, 145.4, 144.7, 143.2, 142.5, 137.0, 132.4, 132.1, 130.0, 129.8, 129.3, 129.2, 124.8, 124.2, 124.0, 122.0, 54.7, 45.8, 35.6, 29.5 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 3223, 3062, 2996, 2853, 1728, 1621, 1567, 1515, 1222; HRMS (ESI$^+$), calcd for $C_{26}H_{21}NO$ (M^+) 364.1696 found 364.1701.

7-chloro-9,13*b*-ethenonaphtho[3,2,1-*kl*]acridin-8(9*H*)-one (3d)



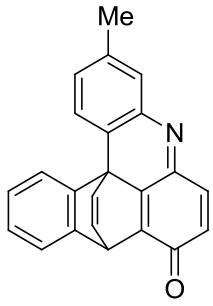
Yield 37% (13 mg), yellow solid, m.p. 196−198 °C; R_f = 0.27 (hexanes/EA = 9 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.96–7.94 (m, 1H), 7.74–7.62 (m, 3H), 7.44–7.40 (m, 2H), 7.07 (t, *J* = 6.2, 1H), 7.02–6.96 (m, 2H), 6.93–6.84 (m, 2H), 5.85 (dd, *J* = 4.4, 1.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 150.8, 147.4, 145.2, 145.1, 145.0, 144.3, 141.9, 137.8, 136.9, 134.5, 133.7, 133.3, 131.0, 129.9, 129.5, 125.2, 124.4, 124.3, 122.3, 55.4, 46.1 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 3255, 3060, 2851, 1774, 1511, 1284, 1051, 1027; HRMS (ESI^+), calcd for $C_{22}H_{12}ClNO$ (M^+) 342.0680 found 342.0686.

2-methyl-9,13*b*-ethenonaphtho[3,2,1-*kl*]acridin-8(9*H*)-one (3e)



Yield 73% (23 mg), yellow solid, m.p. 214−216 °C; R_f = 0.28 (hexanes/EA = 9 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.83 (d, *J* = 8.0, 1H), 7.54 (d, *J* = 0.8, 0.4 Hz, 1H), 7.45–7.39 (m, 2H), 7.22 (d, *J* = 9.6 Hz, 1H), 7.05–6.96 (m, 3H), 6.89–6.88 (m, 2H), 6.54 (d, *J* = 9.6 Hz, 1H), 5.79 (dd, *J* = 4.4, 1.6, 1H), 2.57 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.4, 151.1, 148.1, 145.01, 145.0, 144.7, 143.2, 142.3, 141.5, 137.6, 136.9, 132.9, 132.2, 130.6, 130.2, 129.6, 125.0, 124.2, 124.1, 122.1, 55.3, 45.5, 21.9 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 3225, 3059, 2850, 1693, 1552, 1412, 1315, 1155; HRMS (ESI^+), calcd for $C_{23}H_{15}NO$ (M^+) 322.1226 found 322.1232.

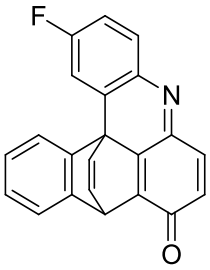
3-methyl-9,13*b*-ethenonaphtho[3,2,1-*kl*]acridin-8(9*H*)-one (3f)



Yield 51% (16 mg), yellow solid, m.p. 218−220 °C; R_f = 0.19 (hexanes/EA = 9 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.76 (s, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.26 (d, *J* = 6.8 Hz, 1H), 7.22 (d, *J* = 10.0 Hz, 1H), 7.04–6.96 (m, 3H), 6.94–6.87 (m, 2H), 6.55 (d, *J* = 9.6 Hz, 1H), 5.79 (d, *J* = 5.6 Hz, 1H), 2.54 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.4, 152.0, 148.1, 145.2, 145.1, 145.0, 144.8, 142.3, 139.3, 137.7, 136.8, 133.5, 132.4, 131.5, 129.7, 126.6, 124.9, 124.2, 124.1, 122.2, 55.0, 45.5, 21.1 ppm; FT-IR

(KBr) $\tilde{\nu}$ (cm^{-1}) 3225, 3062, 2950, 2850, 1729, 1565, 1298, 1156, 1023, 1007; HRMS (ESI^+), calcd for $C_{23}H_{15}NO$ (M^+) 322.1226 found 322.1232.

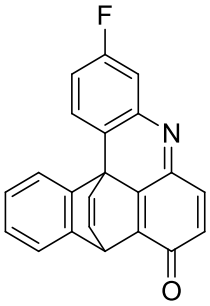
2-fluoro-9,13*b*-ethenonaphtho[3,2,1-*kl*]acridin-8(9*H*)-one (3g)



Yield 79% (26 mg), yellow solid, m.p. 248−250 °C; R_f = 0.13 (hexanes/EA = 9 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.96 (dd, *J* = 5.8, 2.8 Hz, 1H), 7.45–7.40 (m, 2H), 7.35–7.31 (m, 1H), 7.22 (d, *J* = 10.0 Hz, 1H), 7.07–7.02 (m, 1H), 7.01–6.98 (m, 1H), 6.95–6.93 (m, 1H), 6.91–6.88 (m, 2H), 6.56 (d, *J* = 10.0 Hz, 1H), 5.80 (dd, *J* = 4.8, 1.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.2, 164.6 (d, $^1J_{FC}$ = 253.9 Hz), 151.4 (d, $^4J_{FC}$ = 3.5 Hz), 147.5, 145.3, 144.2, 144.2, 142.0, 141.7, 137.5, 137.1, 135.0 (d, $^3J_{FC}$ = 8.7 Hz), 132.5, 132.1 (d, $^3J_{FC}$ = 8.3 Hz), 125.2, 124.4, 124.3, 121.9, 117.0 (d, $^2J_{FC}$ = 23.5 Hz), 116.8 (d, $^2J_{FC}$ = 22.4 Hz), 55.4 (d, $^4J_{FC}$ = 1.9 Hz), 45.6 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 3065, 2954, 2849, 1705, 1627, 1513, 1330, 1275; HRMS (ESI^+), calcd for $C_{22}H_{12}FNO$ (M^+) 326.0976 found 326.0981.

[Note: due to complex splitting, couplings could not be assigned clearly]

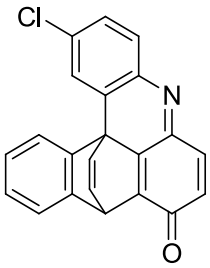
3-fluoro-9,13*b*-ethenonaphtho[3,2,1-*kl*]acridin-8(9*H*)-one (3h)



Yield 52% (17 mg), yellow solid, m.p. 232−234 °C; R_f = 0.21 (hexanes/EA = 9 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.71–7.63 (m, 2H), 7.41–7.34 (m, 2H), 7.22 (d, *J* = 10.0 Hz, 1H), 7.05–6.98 (m, 2H), 6.94–6.83 (m, 3H), 6.57 (d, *J* = 10.0 Hz, 1H), 5.79 (dd, *J* = 4.8, 1.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.4, 163.9 (d, $^1J_{FC}$ = 247.0 Hz), 152.9, 147.8, 146.6 (d, $^3J_{FC}$ = 10.7 Hz), 145.6, 144.7, 144.5, 142.0, 137.5, 136.8, 132.8, 131.0 (d, $^3J_{FC}$ = 8.3 Hz), 125.4 (d, $^4J_{FC}$ = 3.5 Hz), 125.2, 124.4, 124.3, 122.1, 119.2 (d, $^2J_{FC}$ = 21.6 Hz), 117.6 (d, $^2J_{FC}$ = 22.0Hz), 54.9, 45.5 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 3369, 3065, 2954, 2849, 1730, 1700, 1575, 1275, 1110, 1024; HRMS (ESI^+), calcd for $C_{22}H_{12}FNO$ (M^+) 326.0976 found 326.0981.

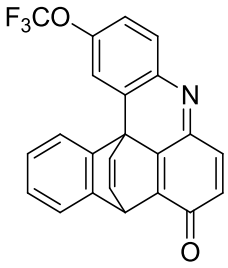
[Note: due to complex splitting, couplings could not be assigned clearly]

2-chloro-9,13*b*-ethenonaphtho[3,2,1-*kl*]acridin-8(9*H*)-one (3i)



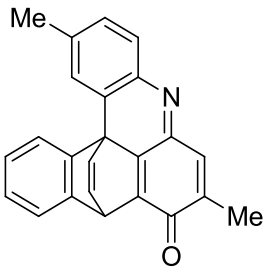
Yield 63% (22 mg), yellow solid, m.p. 192−194 °C; R_f = 0.18 (hexanes/EA = 9 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.88 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 2.4, 1H), 7.61 (dd, *J* = 6.0, 2.2 Hz, 1H), 7.42 (d, *J* = 7.2 Hz, 1H), 7.21 (d, *J* = 9.6 Hz, 1H), 7.06–7.01 (m, 2H), 6.99–6.87 (m, 2H), 6.56 (d, *J* = 9.6 Hz, 1H), 5.79 (d, *J* = 6.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.3, 152.1, 147.5, 145.4, 144.2, 143.7, 141.9 (2C), 137.5, 137.0, 136.3, 134.0, 132.6, 131.2, 129.9, 129.7, 125.3, 124.5, 124.3, 122.0, 55.0, 45.6 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 3434, 3066, 2849, 1703, 1605, 1507, 1408, 1306, 1252; HRMS (ESI$^+$), calcd for $C_{22}H_{12}ClNO$ (M^+) 342.0680 found 342.0686.

2-(trifluoromethoxy)-9,13*b*-ethenonaphtho[3,2,1-*kl*]acridin-8(9*H*)-one (3j)



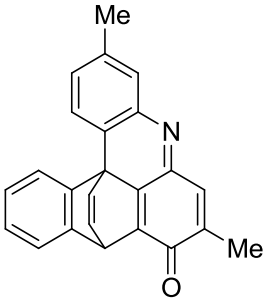
Yield 65% (25 mg), yellow solid, m.p. 182−184 °C; R_f = 0.19 (hexanes/EA = 9 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.99 (d, *J* = 8.8 Hz, 1H), 7.57 (s, 1H), 7.49–7.30 (m, 2H), 7.25 (t, *J* = 11.4 Hz, 1H), 7.07–7.01 (m, 2H), 6.99–6.89 (m, 2H), 6.86 (d, *J* = 7.2 Hz, 1H), 6.57 (d, *J* = 10.0 Hz, 1H), 5.80 (d, *J* = 5.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.2, 152.3, 149.9, 147.4, 145.6, 144.13, 144.1, 143.4, 141.8, 137.5, 137.1, 134.3, 132.7, 135.5 (q, $^1J_{FC}$ = 204.5 Hz), 131.6, 125.3, 124.5, 124.4, 121.9, 121.8, 121.4, 55.2, 45.6 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 3237, 3064, 2849, 1732, 1564, 1517, 1418, 1331, 1255, 1219, 1027, 888; HRMS (ESI$^+$), calcd for $C_{23}H_{12}F_3NO_2$ (M^+) 392.0893 found 392.0888.

2,7-dimethyl-9,13*b*-ethenonaphtho[3,2,1-*kl*]acridin-8(9*H*)-one (3k)



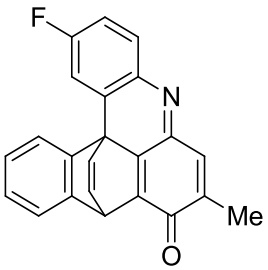
Yield 60% (20 mg), yellow solid, m.p. 194−196 °C; R_f = 0.24 (hexanes/EA = 9 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.80 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 1.6 Hz, 1H), 7.43–7.32 (m, 2H), 7.04–7.01 (m, 2H), 6.99–6.94 (m, 2H), 6.89–6.85 (m, 2H), 5.80 (dd, *J* = 4.4, 1.6 Hz, 1H), 2.56 (s, 3H), 2.08 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.7, 151.2, 148.2, 144.9, 144.63, 144.61, 143.3, 142.6, 140.83, 140.8, 137.0, 133.8, 132.5, 130.5, 130.1, 129.4, 124.9, 124.1, 124.0, 122.1, 55.1, 45.7, 21.8, 16.3 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 3062, 2953, 2849, 1701, 1577, 1512, 1221; HRMS (ESI^+), calcd for $C_{24}H_{17}NO$ (M^+) 336.1383 found 336.1388.

3,7-dimethyl-9,13*b*-ethenonaphtho[3,2,1-*kl*]acridin-8(9*H*)-one (3l)



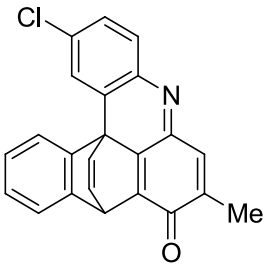
Yield 46% (15 mg), yellow solid, m.p. 214−216 °C; R_f = 0.27 (hexanes/EA = 9 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.73 (s, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.44 (dd, *J* = 7.4 Hz, 2H), 7.03–6.84 (m, 6H), 5.79 (d, *J* = 5.2 Hz, 1H), 2.53 (s, 3H), 2.08 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.7, 152.0, 148.2, 145.2, 145.1, 144.8, 144.7, 142.6, 141.0, 139.1, 136.9, 133.9, 133.1, 130.9, 129.6, 126.4, 124.9, 124.1, 124.0, 122.1, 54.8, 45.7, 21.1, 16.3 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 3219, 3061, 3005, 2854, 1915, 1514, 1374, 1300, 1264, 1171, 1023, 882; HRMS (ESI^+), calcd for $C_{24}H_{17}NO$ (M^+) 336.1383 found 336.1388.

2-fluoro-7-methyl-9,13*b*-ethenonaphtho[3,2,1-*kl*]acridin-8(9*H*)-one (3m)



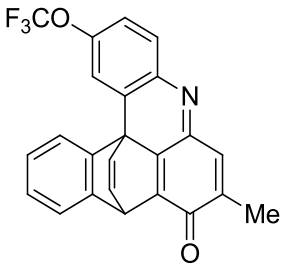
Yield 42% (14 mg), yellow solid, m.p. 242−244 °C; R_f = 0.22 (hexanes/EA = 9 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.92 (dd, *J* = 6.0, 2.8 Hz, 1H), 7.43–7.39 (m, 2H), 7.33–7.28 (m, 1H), 7.06–6.96 (m, 3H), 6.93–6.87(m, 3H), 5.81 (dd, *J* = 4.4, 1.6 Hz, 1H), 2.08 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.5, 164.2 (d, $^1J_{FC}$ = 252.7 Hz), 151.4 (d, $^4J_{FC}$ = 3.4 Hz), 147.6, 145.2 (d, $^5J_{FC}$ = 1.6 Hz), 144.0, 143.9, 142.3, 141.90 (d, $^4J_{FC}$ = 3.5 Hz), 141.86, 137.3, 134.5 (d, $^3J_{FC}$ = 8.7 Hz), 133.7, 131.8 (d, $^3J_{FC}$ = 8.3 Hz), 125.1, 124.3, 124.2, 121.8, 116.9 (d, $^2J_{FC}$ = 23.5 Hz), 116.7 (d, $^2J_{FC}$ = 22.4 Hz), 55.2, 45.8, 16.3 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 3063, 2918, 2849, 1733, 1621, 1569, 1310, 1271; HRMS (ESI$^+$), calcd for $C_{23}H_{14}FNO$ (M^+) 340.1132 found 340.1137.

2-chloro-7-methyl-9,13*b*-ethenonaphtho[3,2,1-*kl*]acridin-8(9*H*)-one (3n)



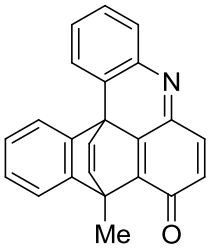
Yield 61% (22 mg), yellow solid, m.p. 222−224 °C; R_f = 0.24 (hexanes/EA = 9 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.86 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 2.4, 1H), 7.59 (dd, *J* = 6.4, 2.0 Hz, 1H), 7.41 (d, *J* = 7.2 Hz, 1H), 7.06–6.98 (m, 3H), 6.97–6.87 (m, 3H), 5.80 (d, *J* = 6.0 Hz, 1H), 2.80 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.6, 152.2, 147.6, 145.4, 144.1, 143.9, 143.7, 142.2, 141.5, 137.2, 135.7, 133.5, 133.5, 131.1, 129.9, 129.6, 125.2, 124.34, 124.30, 122.0, 54.8, 45.8, 16.3 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 3060, 2953, 2849, 1730, 1577, 1509, 1374; HRMS (ESI$^+$), calcd for $C_{23}H_{14}ClNO$ (M^+) 356.0837 found 356.0842.

7-methyl-2-(trifluoromethoxy)-9,13*b*-ethenonaphtho[3,2,1-*kl*]acridin-8(9*H*)-one (3o)



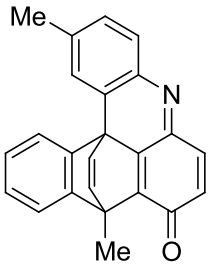
Yield 59% (24 mg), yellow solid, m.p. 216−218 °C; R_f = 0.26 (hexanes/EA = 9 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95 (d, *J* = 8.8 Hz, 1H), 7.56 (s, 1H), 7.47–7.40 (m, 2H), 7.07–6.98 (m, 3H), 6.94–6.83 (m, 3H), 5.81 (d, *J* = 6.0 Hz, 1H), 2.09 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.5, 152.4, 149.5, 147.5, 145.5, 144.0, 143.8, 143.6, 142.1, 141.6, 137.3, 133.9, 133.6, 131.3, 128.5 (q, $^1J_{FC}$ = 247.4 Hz), 125.2, 124.4, 124.3, 121.9, 121.8, 121.4, 55.0, 45.8, 16.3 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 3067, 2954, 2849, 1704, 1615, 1569, 1507, 1407, 1361, 1256, 1173, 1023, 888; HRMS (ESI$^+$), calcd for $C_{24}H_{14}F_3NO_2$ (M^+) 406.1049 found 406.1055.

9-methyl-9,13*b*-ethenonaphtho[3,2,1-*kl*]acridin-8(9*H*)-one (3p)



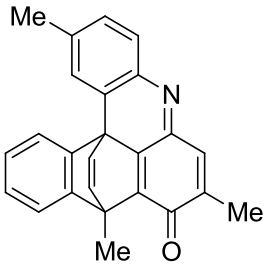
Yield 72% (23 mg), dark yellow solid, m.p. 202−204 °C; R_f = 0.23 (hexanes/EA = 9 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.93–7.91 (m, 1H), 7.70–7.68 (m, 1H), 7.65–7.61 (m, 2H), 7.44 (dd, *J* = 0.6, 6.8, 1H), 7.17 (d, *J* = 10.0 Hz, 1H), 7.08–7.04 (m, 1H), 6.96 (d, *J* = 6.4 Hz, 1H), 6.91–6.82 (m, 2H), 6.68 (d, *J* = 6.4 Hz, 1H), 6.44 (d, *J* = 10.0, 1H), 2.48 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.0, 151.8, 148.7, 147.1, 145.5, 145.0, 144.7, 144.5, 142.8, 136.8, 133.7, 132.6, 130.4, 129.9, 129.8, 129.3, 124.9, 123.9, 122.0, 121.7, 55.0, 52.6, 17.0 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 3369, 3226, 3062, 2851, 1912, 1510, 1477, 1412, 1375, 1306, 1172, 1090, 1048, 1010, 992; HRMS (ESI^+), calcd for $C_{23}H_{15}NO$ (M^+) 322.1226 found 322.1232.

2,9-dimethyl-9,13*b*-ethenonaphtho[3,2,1-*kl*]acridin-8(9*H*)-one (3q)



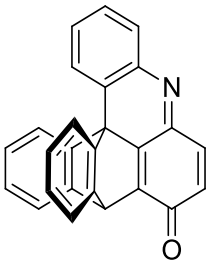
Yield 50% (17 mg), yellow solid, m.p. 254−256 °C; R_f = 0.19 (hexanes/EA = 9 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.81 (d, *J* = 8.0 Hz, 1H), 7.49 (s, 1H), 7.43 (d, *J* = 7.6 Hz, 2H), 7.15 (d, *J* = 9.6 Hz, 1H), 7.07 (t, *J* = 7.0 Hz, 1H), 6.95 (d, *J* = 6.4 Hz, 1H), 6.91–6.84 (m, 2H), 6.67 (d, *J* = 6.4 Hz, 1H), 6.42 (d, *J* = 9.6 Hz, 1H), 2.56 (s, 3H), 2.47 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.0, 150.9, 148.7, 147.2, 145.7, 144.7, 144.5, 142.9, 142.7, 141.3, 136.8, 133.4, 132.5, 130.5, 130.1, 129.8, 124.9, 123.8, 121.9, 121.6, 54.9, 52.6, 21.9, 17.0 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 3294, 3063, 2954, 2849, 1729, 1703, 1616, 1574, 1507, 1462, 1288, 1255, 1219, 1025; HRMS (ESI^+), calcd for $C_{24}H_{17}NO$ (M^+) 336.1383 found 336.1388.

2,7,9-trimethyl-9,13*b*-ethenonaphtho[3,2,1-*kl*]acridin-8(9*H*)-one (3r)



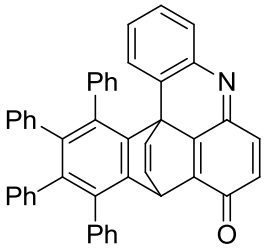
Yield 58% (20 mg), yellow solid, m.p. 222−224 °C; R_f = 0.27 (hexanes/EA = 9 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.79 (d, *J* = 8.0 Hz, 1H), 7.48 (s, 1H), 7.43–7.39 (m, 2H), 7.07–7.03 (m, 1H), 6.99 (d, *J* = 1.2 Hz, 1H), 6.94 (d, *J* = 6.4 Hz, 1H), 6.90–6.83 (m, 2H), 6.67 (d, *J* = 6.4 Hz, 1H), 2.55 (s, 3H), 2.48 (s, 3H), 2.03 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.3, 150.9, 148.7, 146.9, 145.9, 144.6, 144.4, 143.0, 142.8, 141.4, 140.6, 133.3, 132.1, 130.4, 130.0, 129.6, 124.8, 123.7, 121.9, 121.5, 54.7, 52.7, 21.8, 17.2, 16.4 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 3220, 2923, 2853, 1737, 1620, 1559, 1260; HRMS (ESI$^+$), calcd for $C_{25}H_{19}NO$ (M^+) 350.1539 found 350.1545.

9,13*b*-[1,2]benzenonaphtho[3,2,1-*kl*]acridin-8(9*H*)-one (3s)



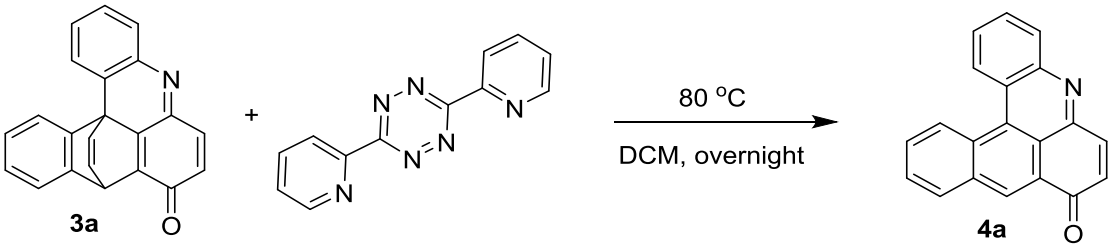
Yield 76% (27 mg), yellow solid, m.p. 252−254 °C; R_f = 0.19 (hexanes/EA = 9 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.06 (dd, *J* = 6.4, 1.2 Hz, 1H), 7.09 (dd, *J* = 5.6, 1.6 Hz, 1H), 7.77–7.70 (m, 2H), 7.57 (d, *J* = 7.2 Hz, 2H), 7.24 (d, *J* = 10.0 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 2H), 6.98 (t, *J* = 7.4 Hz, 2H), 6.57 (d, *J* = 9.6 Hz, 1H), 6.07 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.6, 152.3, 145.7, 145.6, 145.5, 144.3, 141.5, 138.1, 133.8, 132.5, 132.1, 129.74, 129.7, 126.0, 125.5, 125.0, 124.9, 123.1, 54.7, 47.3 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 3229, 2981, 2921, 1630, 1515, 1329, 1247; HRMS (ESI$^+$), calcd for $C_{26}H_{15}NO$ (M^+) 358.1226 found 358.1231.

10,11,12,13-tetraphenyl-9,13*b*-ethenonaphtho[3,2,1-*kl*]acridin-8(9*H*)-one (3t)



Yield 70% (43 mg), yellow solid, m.p. 270−272 °C; R_f = 0.14 (hexanes/EA = 9 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.58 (d, *J* = 8.0 Hz, 1H), 7.36–7.28 (m, 3H), 7.23–7.19 (m, 2H), 7.09–7.00 (m, 3H), 6.93–6.84 (m, 4H), 6.77–6.714 (m, 4H), 6.73–6.62 (m, 4H), 6.59–6.47 (m, 5H), 6.26 (d, *J* = 7.6, 2H), 5.76 (dd, *J* = 4.8, 1.4, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.0, 151.5, 146.7, 145.9, 145.4, 144.1, 143.3, 140.7, 139.92, 139.86, 139.0, 138.3, 138.0, 137.78, 137.76, 137.4, 136.5, 132.3, 131.7, 131.4, 131.3, 131.1, 131.0, 130.96, 130.7, 130.5, 130.3, 130.2, 130.1, 128.2, 128.0, 127.5, 127.4, 126.8, 126.6, 126.3, 126.21, 126.20, 126.1, 125.9, 125.3, 124.9, 56.2, 44.2 ppm (more ^{13}C signals were observed due to hindered rotation of phenyl groups); FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 3079, 3055, 3024, 2954, 2918, 2850, 1945, 1877, 1801, 1707, 1624, 1573, 1510, 1408, 1023; HRMS (ESI^+), calcd for $C_{46}H_{29}NO$ (M^+) 612.2322 found 612.2328.

K. Synthesis of 8*H*-naphtho[3,2,1-*kl*]acridin-8-one (4a)[6]

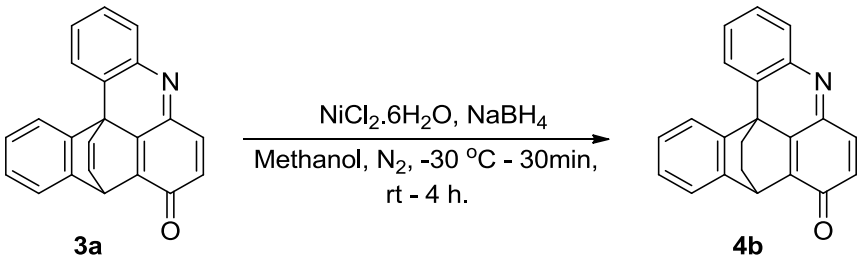


A 15 mL pressure tube equipped with a stirring bar was charged 9,13b-ethenonaphtho[3,2,1-kl]acridin-8(9H)-one **3a** (0.1 mmol, 30.7 mg), 3,6-di(pyridin-2-yl)-1,2,4,5-tetrazine (0.15 mmol, 35.0 mg) and DCM (1.0 mL) was added in presence of air atmosphere. Then, the resulting mixture was heated for overnight at 80 °C with stirring. Upon completion of the reaction, the reaction mixture was concentrated and washed with methanol several time. The precipitate was dried through vacuum to remove the methanol completely to afford product **4a**. Yield 90% (25 mg), yellow solid, m.p. 110−112 °C; R_f = 0.31 (hexanes/EA = 1 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.01 (d, *J* = 8.4 Hz, 1H), 8.87 (d, *J* = 8.4 Hz, 1H), 8.78 (s, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 10.0 Hz, 1H), 7.82–7.76 (m, 2H), 7.74–7.69 (m, 2H), 6.93 (d, *J* = 10.0 Hz, 1H) pm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.1, 148.3, 146.7, 144.6, 133.7, 133.2, 132.3, 131.8, 131.2, 131.1, 130.4, 129.9, 129.0, 128.5, 128.3, 128.1, 126.7, 125.8, 124.0, 120.1 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 3053, 2954, 2916, 2849, 1705, 1608, 1584, 1569, 1462, 1380, 1270, 1246, 1085, 1048; HRMS (ES), calcd for $C_{20}H_{11}NO$ (M) 281.0840 found 281.0843.

L. Synthesis of 9,13*b*-ethanonaphtho[3,2,1-*kl*]acridin-8(9*H*)-one[7]

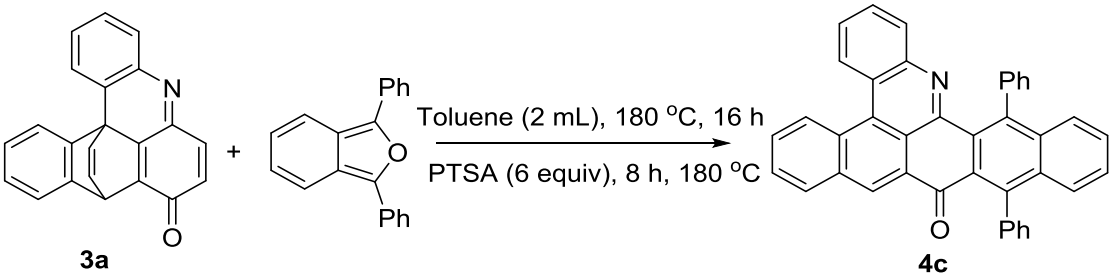
---

[6] Gomez-Bengoa, E.; Helm, M. D.; Plant, A.; Harrity, J. P. A., *J. Am. Chem. Soc.* **2007,** *129*, 2691.



A 15 mL round bottom flask equipped with a stirring bar was charged 9,13b-ethenonaphtho[3,2,1-kl]acridin-8(9H)-one **3a** (0.1 mmol, 30.7 mg), $NiCl_2.6H_2O$ (0.2 mmol, 47.5 mg) and methanol (2.0 mL) was added under of N_2 atmosphere. Then, the resulting mixture kept stirring at -30 °C for 30 min. To this stirred contents, $NaBH_4$ (10 mmol, 37.8 mg) was dissolved in methanol and added slowly. The reaction mixture was further stirred for 30 min at -30 °C and 4h at room temperature. 3N NaOH solution (5 mL) was added followed by ether (10 mL) and the mixtures were filtered. The organic layer was washed with brine solution (3 X 10 mL), dried over anhydrous Na_2SO_4 and solvent removed under reduced pressure. The crude product was purified by flash chromatography on silica gel to afford 9,13b-ethanonaphtho[3,2,1-kl]acridin-8(9H)-one (**4b**). Yield 74% (23 mg), yellow solid, m.p. 196−198 °C; R_f = 0.19 (hexanes/EA = 9 : 1); ^{1}H NMR ($CDCl_3$, 700 MHz) δ 7.90 (d, *J* = 7.7 Hz, 1H), 7.75 (d, *J* = 7.0 Hz, 1H), 7.58–7.54 (m, 2H), 7.39 (d, *J* = 7.0 Hz, 1H), 7.30 (d, *J* = 9.8 Hz, 1H), 7.15–7.13 (m, 1H), 7.06 (d, *J* = 4.2 Hz, 2H), 6.62 (d, *J* = 9.8 Hz, 1H), 4.95 (s, 1H), 2.19–2.15 (m, 1H), 7.74–1.84 (t, *J* = 10.5 Hz, 1H), 1.61–1.53 (m, 1H), 1.50 (t, *J* = 5.6 Hz, 1H) ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 182.8, 151.7, 144.6, 142.7, 141.4, 140.7, 139.9, 138.5, 133.0, 132.8, 130.6, 129.9, 129.2, 128.8, 126.4, 125.5, 124.5, 122.5, 45.8, 37.2, 34.8, 22.7 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 2953, 2849, 1730, 1699, 1632, 1569, 1516, 1466, 1446, 1408, 1288, 1214, 1027, 836; HRMS (ESI$^+$), calcd for $C_{22}H_{15}NO$ (M^+) 310.1226 found 310.1232.

M. Synthesis of 11,16-diphenyl-10*H*-dinaphtho[2,3-*c*:1',2',3'-*mn*]acridin-10-one (4c)[8]



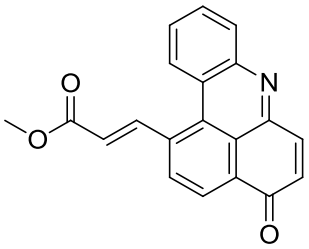
---

[7] Periasamy, M.; Devasagayaraj, A.; Satyanarayana, N.; Narayana, C., *Synth. Commun.* **1989,** *19*, 565.

[8] Zhou, L.; Xu, B.; Zhang, J., *Angew.Chem. Int.Ed.* **2015,** *54*, 9092.

A 15 mL pressure tube equipped with a stirring bar was charged 9,13b-ethenonaphtho[3,2,1-*kl*]acridin-8(9*H*)-one **3a** (0.1 mmol, 30.7 mg), 1,3-diphenylisobenzofuran (0.25 mmol, 67.5 mg) and toluene (2 mL) was added in the air atmosphere and degassed using N_2 for 5 min. Then, the resulting mixture kept stirring at 180 ^oC for 16 h. Further, the reaction cool to room temperature. To this stirred mixtures, PTSA (0.6 mmol, 172.2 mg) was added. The reaction mixture was kept stirring at 180 ^oC for 10 h. Upon cooling down to room temperature, the reaction mixture was workup with $NaHCO_3$ solution (10 mL X 3) and extracted with ethyl acetate and the mixture was filtered and dried over Na_2SO_4. The filtrate was concentrated in vacuum, and then the residue was purified by flash chromatography (eluent: hexane: ethyl acetate = 9:1) to afford products **4c**. Yield 68% (36 mg), yellow solid, m.p. 196−198 ^oC; R_f = 0.35 (hexanes/EA = 9 : 1); ^1H NMR ($CDCl_3$, 400 MHz) δ 9.13 (d, *J* = 8.4 Hz, 1H), 8.92–8.88 (m, 2H), 8.18 (d, *J* = 8.0 Hz, 1H), 7.85 (t, *J* = 7.6 Hz, 2H), 7.78 (t, *J* = 7.4 Hz, 1H), 7.63–7.52 (m, 9H), 7.50–7.40 (m, 7H) pm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 184.9, 148.2, 144.6, 144.0, 143.1, 141.7, 141.3, 136.4, 134.1, 133.9, 131.3, 131.1, 131.0, 130.8, 130.5, 130.2, 129.3, 128.8, 128.7, 128.5, 128.4, 128.3, 128.21, 128.2, 127.9, 127.7, 127.4, 127.3, 126.9, 126.4, 126.1, 122.9, 120.6 ppm (three fewer ^{13}C signals were observed due to coincidental overlaps); FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 2954, 2917, 2849, 1702, 1606, 1506, 1462, 1407, 1362, 1295, 1254, 1200, 1151; HRMS (ESI^+), calcd for $C_{40}H_{23}NO$ (M^+) 534.1852 found 534.1857.

N. Synthesis of (*E*)-methyl 3-(5-(2-((4-oxocyclohexa-2,5-dien-1-ylidene)amino)phenyl)furan-2-yl)acrylate (4d)



A 15 mL pressure tube equipped with a stirring bar was charged with 4-((2-(furan-2-yl)phenyl)imino)cyclohexa-2,5-dienone (0.1mmol, 24.9 mg), $Pd(OAc)_2$ (0.01mmol, 2.24 mg), $Cu(OAc)_2$ (0.05mmol, 9.08 mg) and 0.5 mL of TFEtOH was added in air atmosphere. Then, the reaction tube closed with septum and purged O_2 (1 atm) gas for 30 sec. Further, methylacrylate (0.3mmol, 25.8 mg) in 0.5 mL of TFEtOH was injected into reaction mixture by a syringe. After septeum was removed and closed with a Teflon cap, then reaction mixture was heated for 24 h at 120 ^oC with stirring. Upon cooling down to room temperature, the reaction mixture was diluted with 10 mL of ethyl acetate followed by filtration through a thin pad of celite. The filtrate was concentrated in vacuum, and then the residue was purified by thin layer chromatography (eluent: hexanes:ethyl acteate = 7:3) to

afford product **4d**. Yield 42% (14 mg), yellow solid, m.p. 242−246 °C; R_f = 0.53 (hexanes/EA = 7 : 3); ^{1}H NMR (DCM-d_2, 400 MHz) δ 8.52–8.47 (m, 3H), 8.30 (d, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 7.6 Hz, 1H), 7.91–7.84 (m, 2H), 7.81–7.76 (m, 1H), 6.95 (d, *J* = 10.0 Hz, 1H), 6.64 (d, *J* = 16.0, 1H), 3.91 (s, 3H) ppm; ^{13}C NMR (100 MHz, DCM-d_2) δ 184.7, 166.4, 149.8, 146.1, 145.7, 143.8, 139.3, 133.0, 132.1, 131.6, 130.2, 129.6, 129.5, 128.9, 127.8, 127.4, 123.8, 122.4, 122.3, 52.0 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 3739, 2961, 2926, 2873, 1573, 1249, 1090; HRMS (ESI$^+$), calcd for $C_{20}H_{13}NO_4$ (M^+) 334.1074 found 334.1074.

Figure S01. ^{1}H-NMR spectrum of compound **1a** ($CDCl_3$,400 MHz)

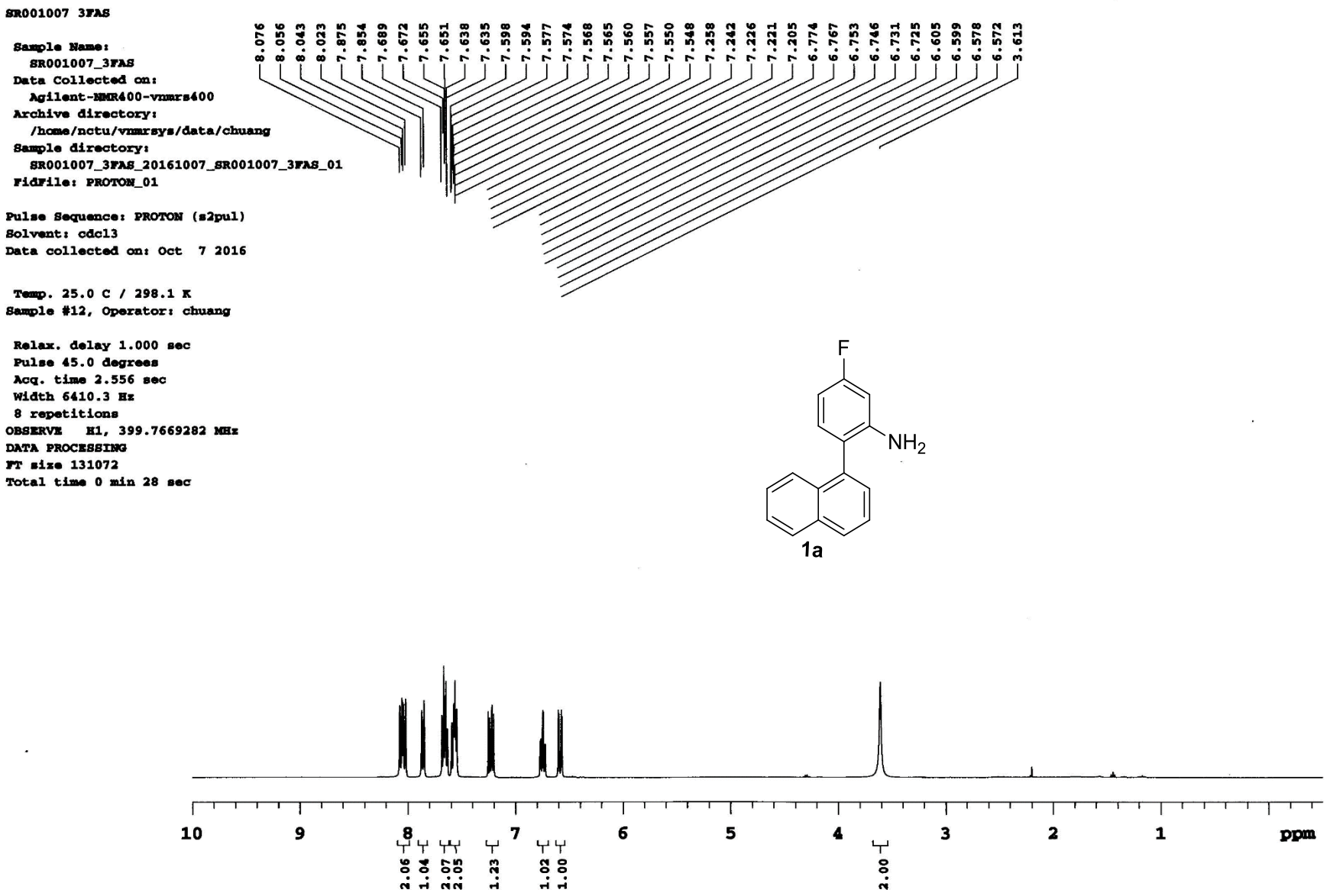


Figure S02. ^{13}C-NMR spectrum of compound **1a** ($CDCl_3$,100 MHz)

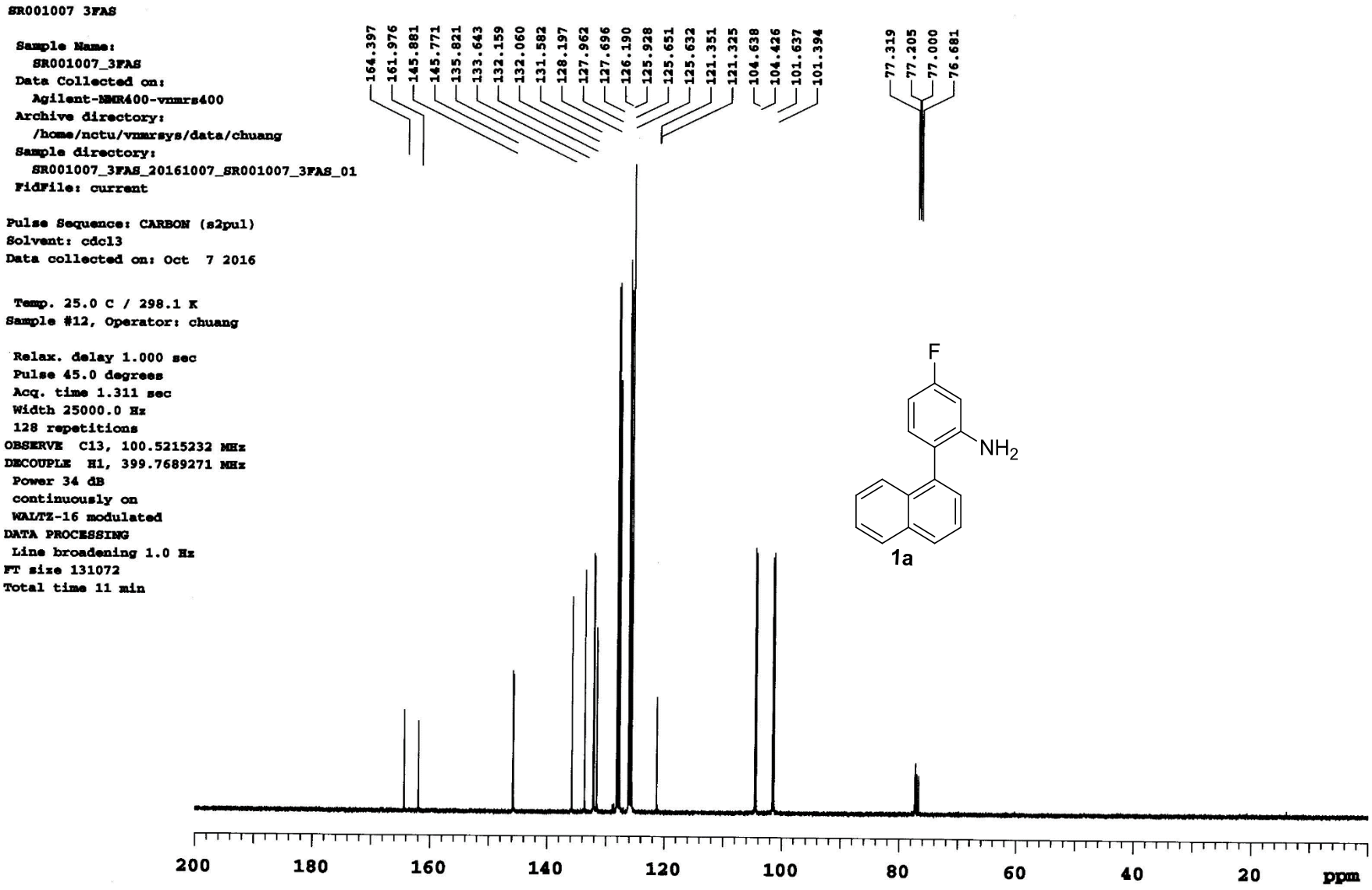


Figure S03. ^{1}H-NMR spectrum of compound **1b** ($CDCl_3$,400 MHz)

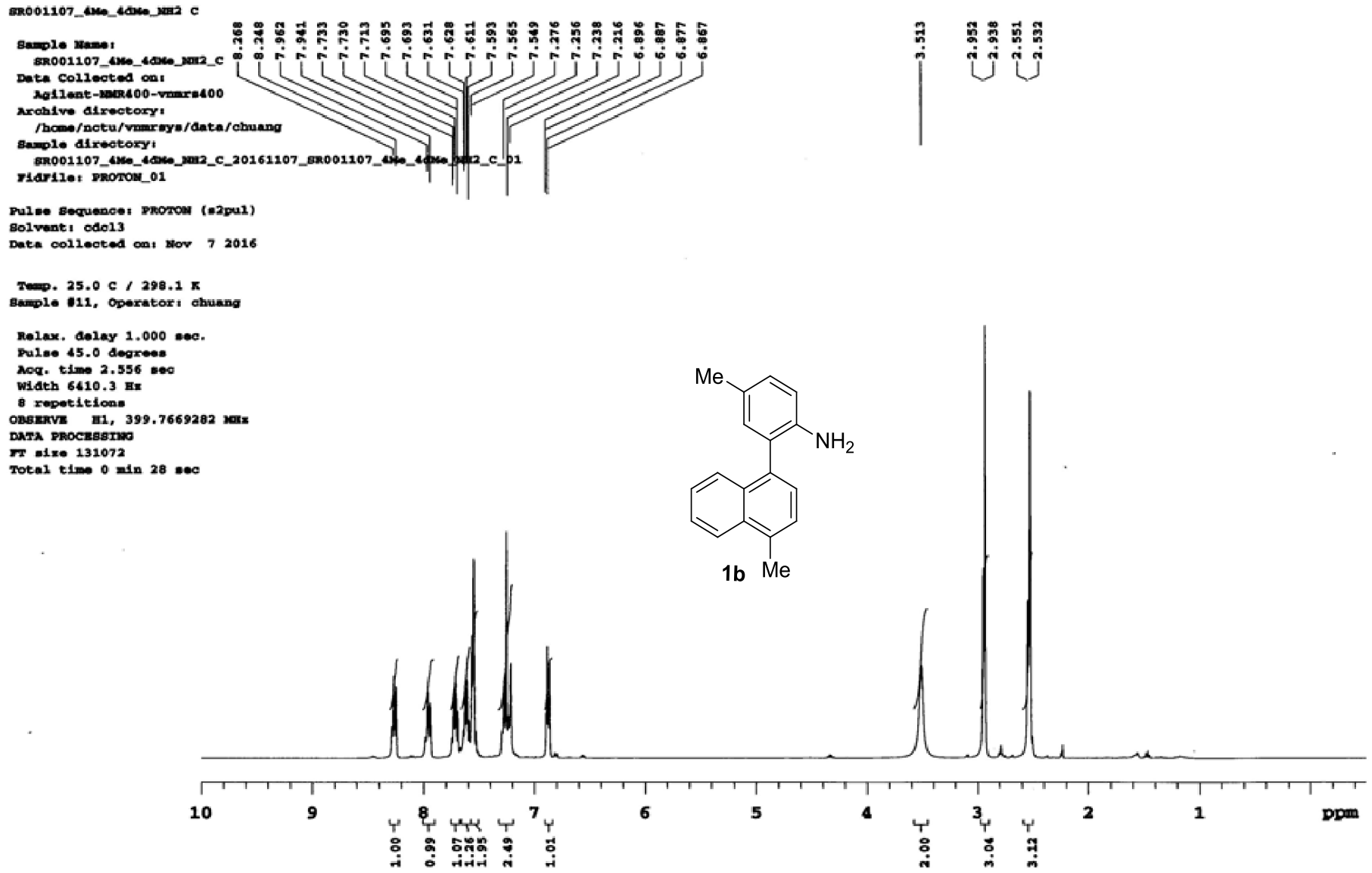


Figure S04. ^{13}C-NMR spectrum of compound **1b** ($CDCl_3$,100 MHz)

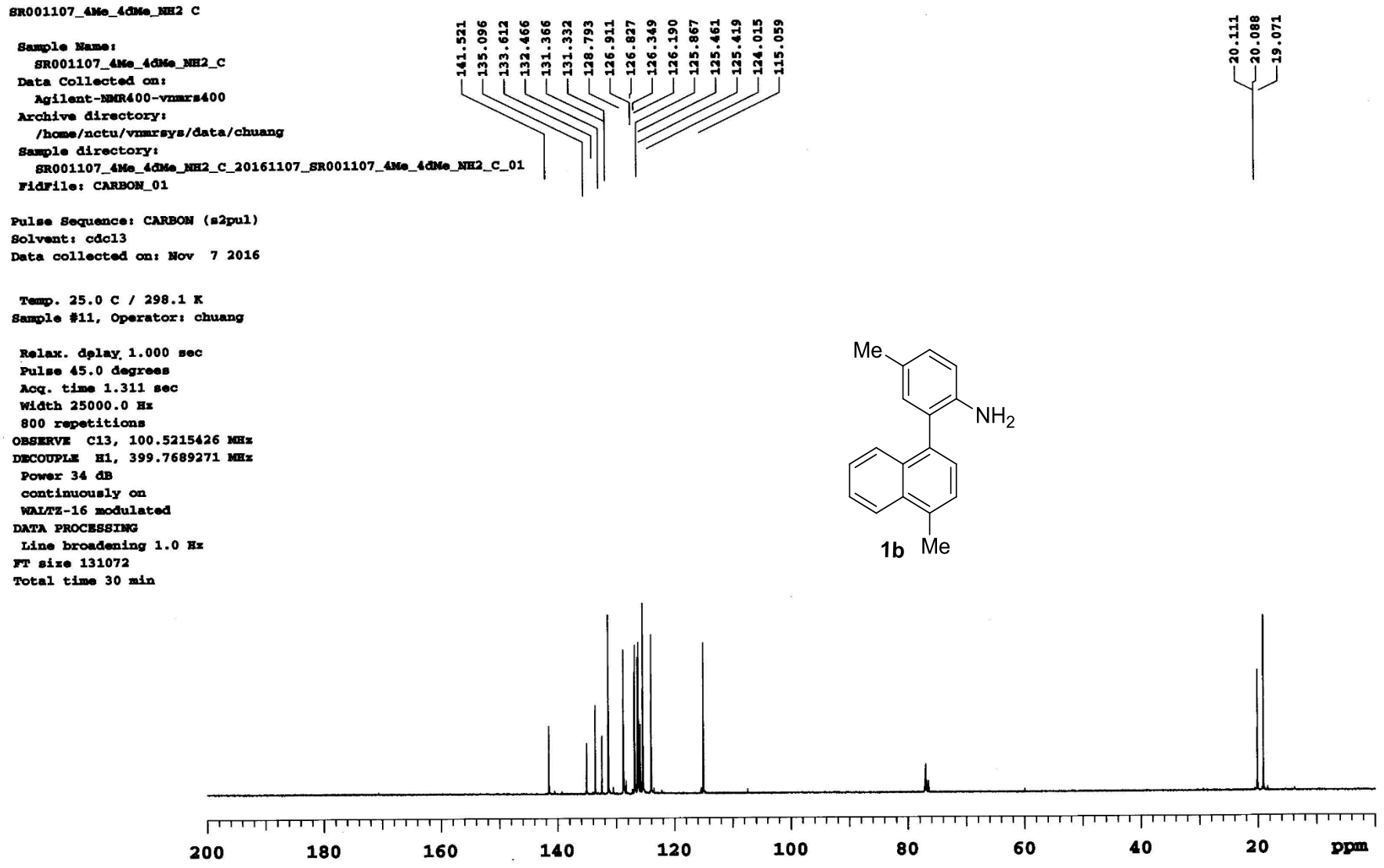


Figure S05. ^{1}H-NMR spectrum of compound **1c** ($CDCl_3$,400 MHz)

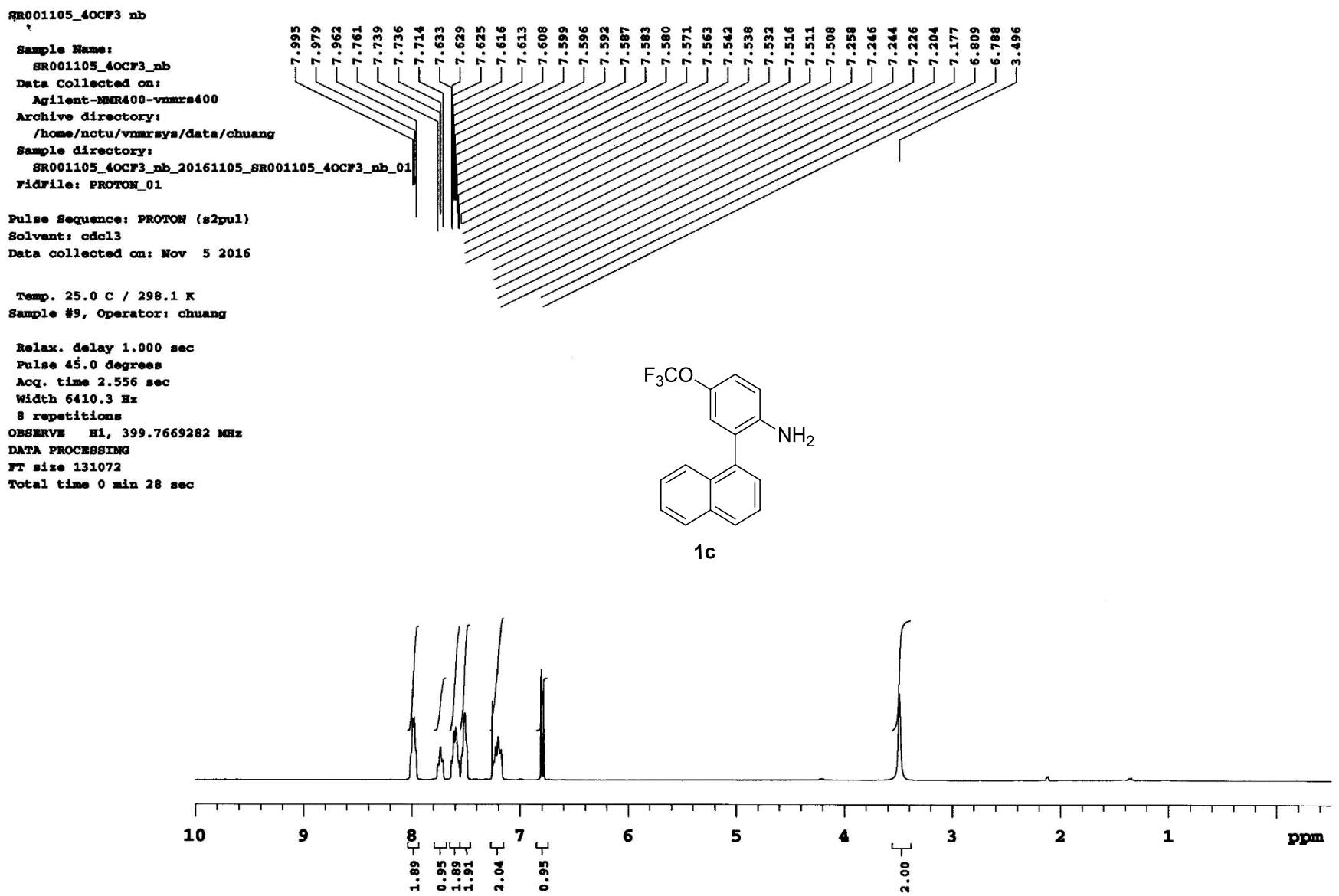


Figure S06. ^{13}C-NMR spectrum of compound **1c** ($CDCl_3$,100 MHz)

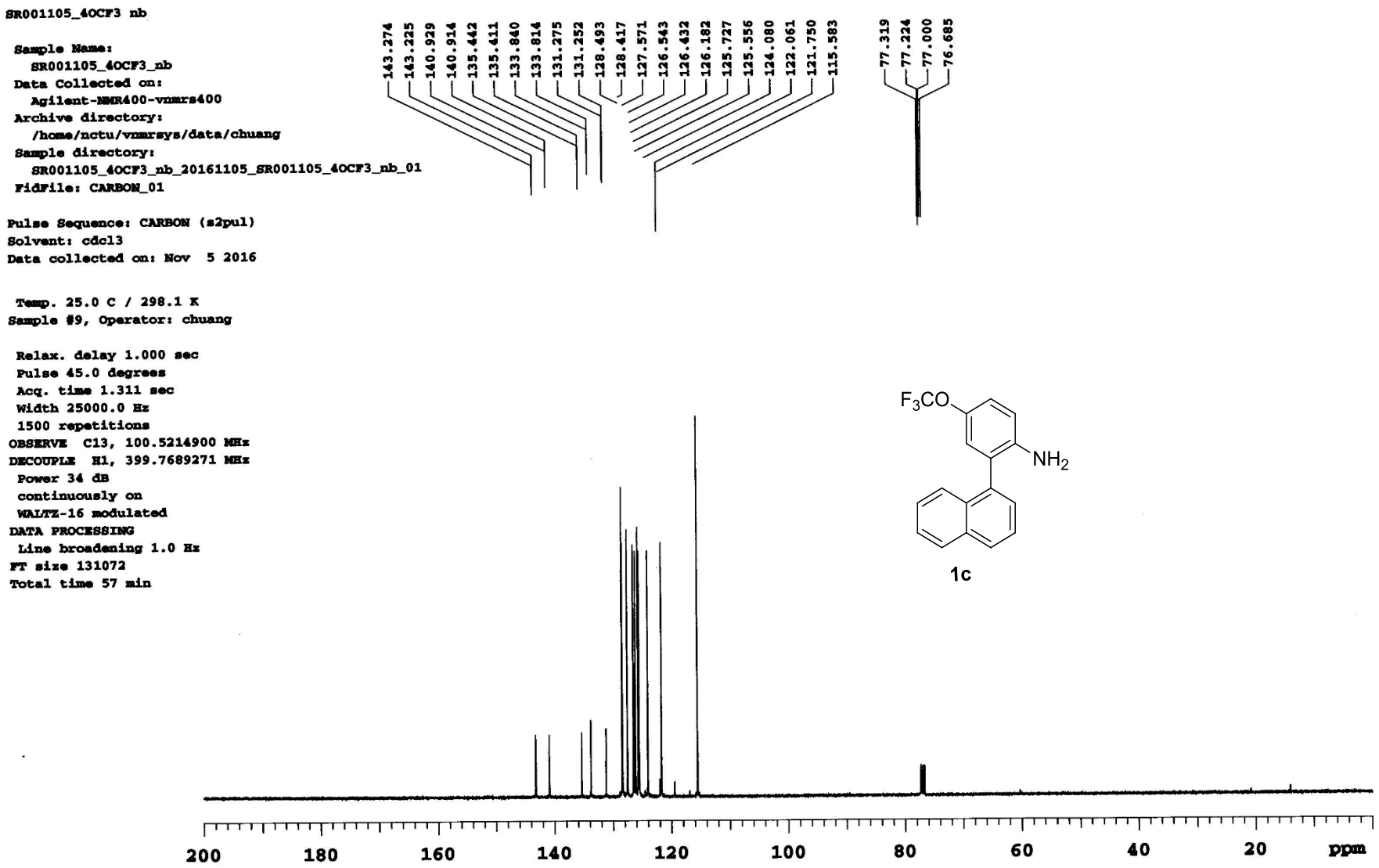


Figure S07. ^{13}C-NMR spectrum of compound **1d** ($CDCl_3$,100 MHz)

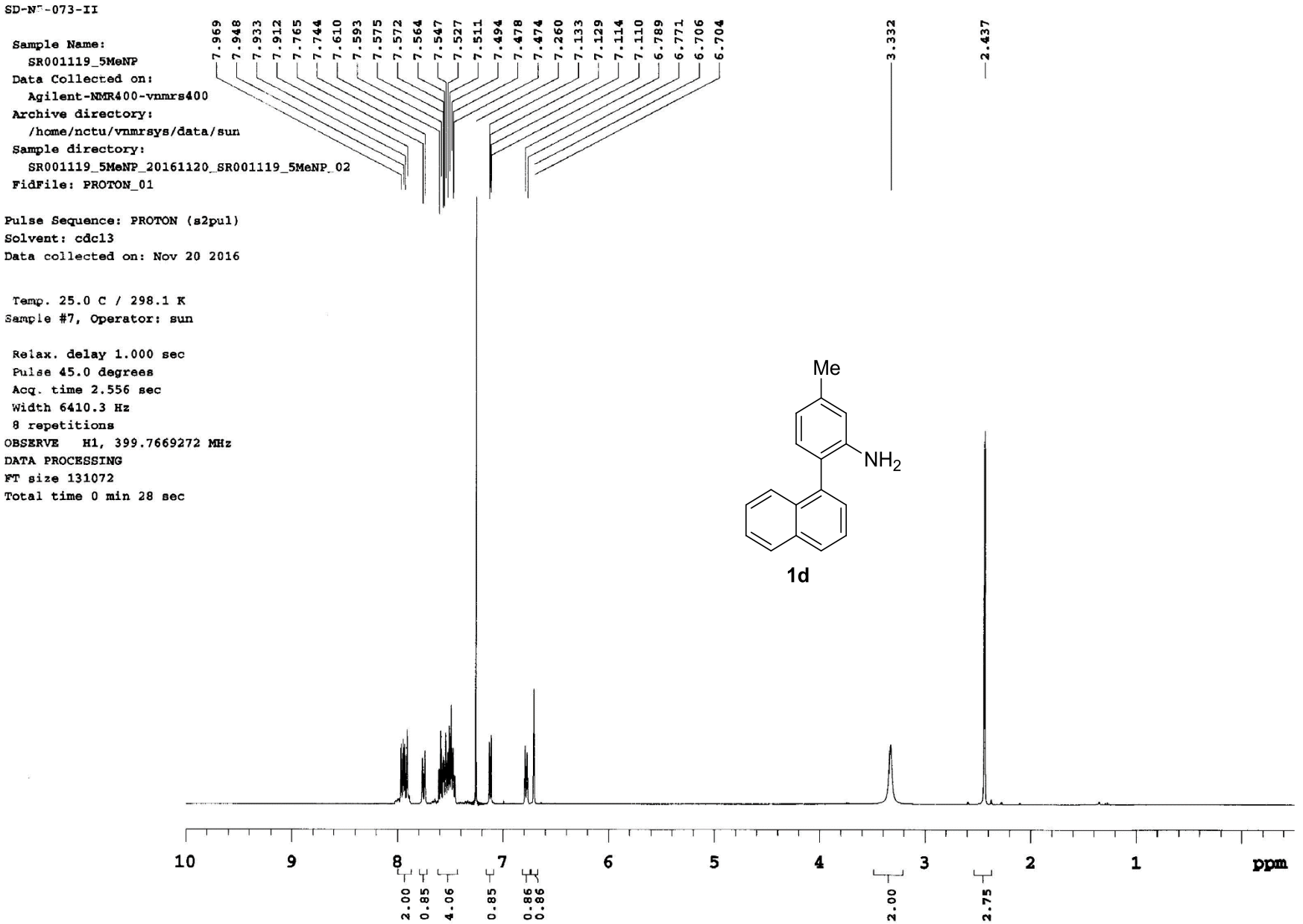


Figure S08. ^{13}C-NMR spectrum of compound **1d** ($CDCl_3$,100 MHz)

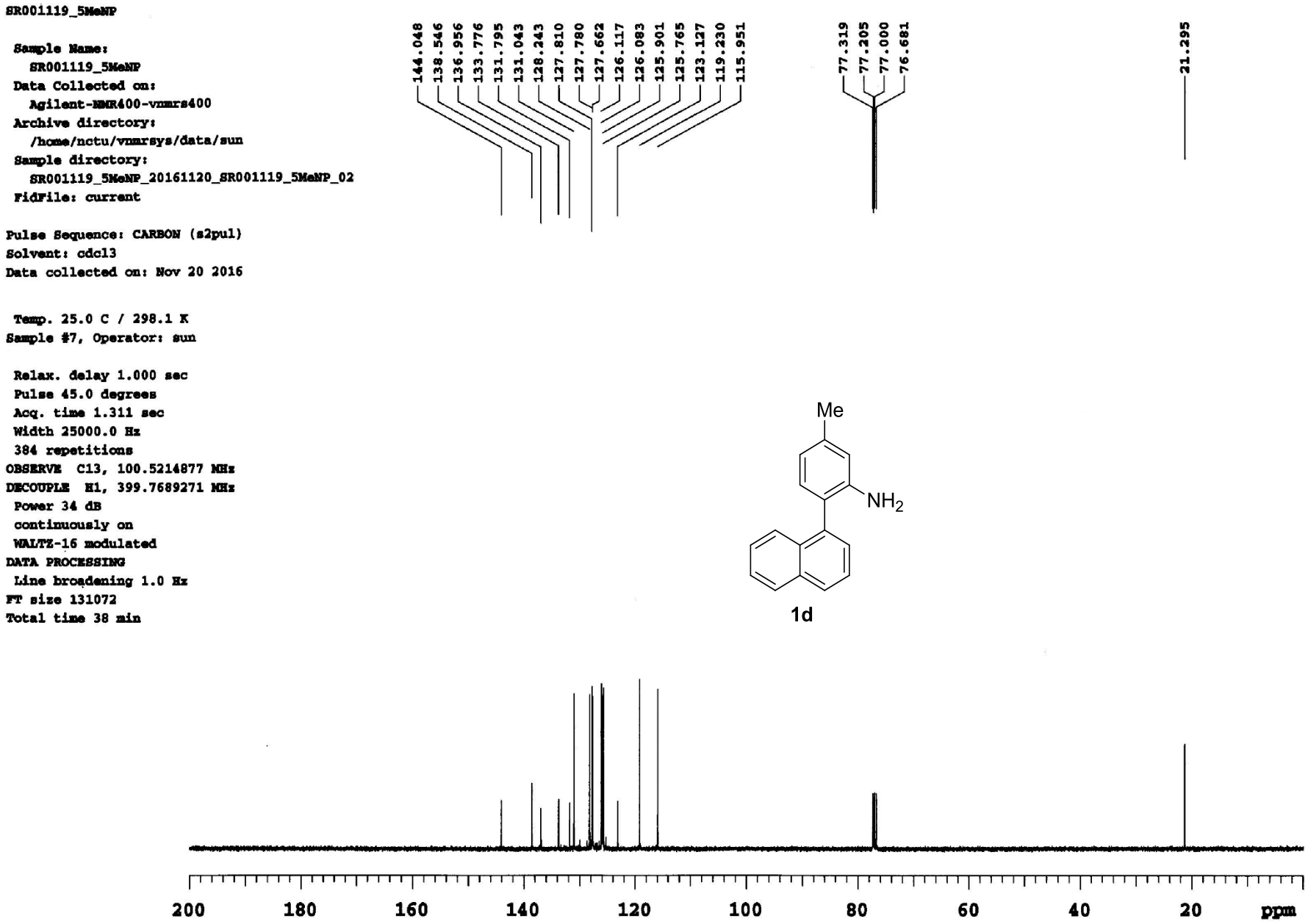


Figure S09. ^{13}C-NMR spectrum of compound **E-4** ($CDCl_3$,400 MHz)

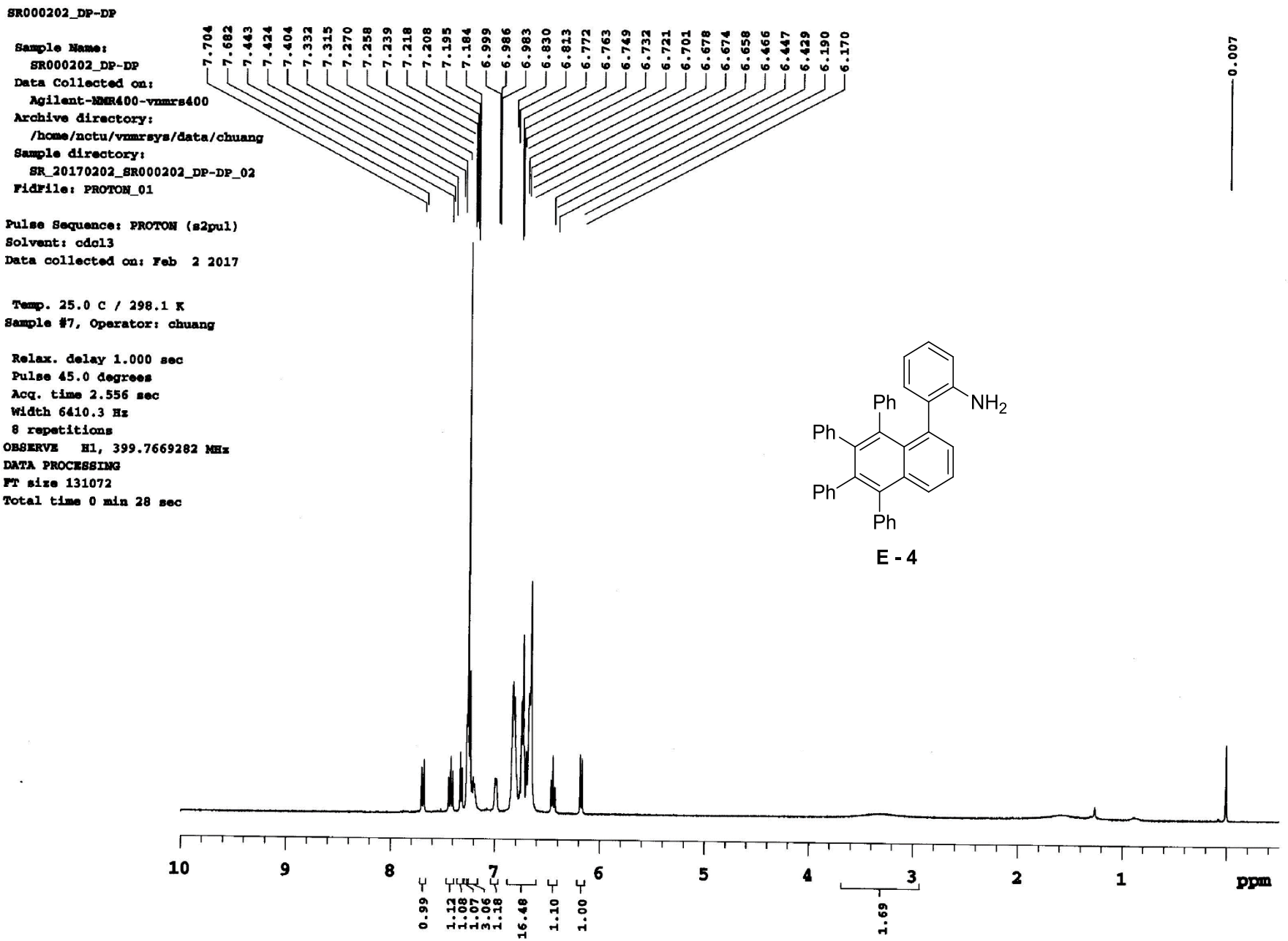


Figure S10. ^{13}C-NMR spectrum of compound **E-4** ($CDCl_3$,400 MHz)

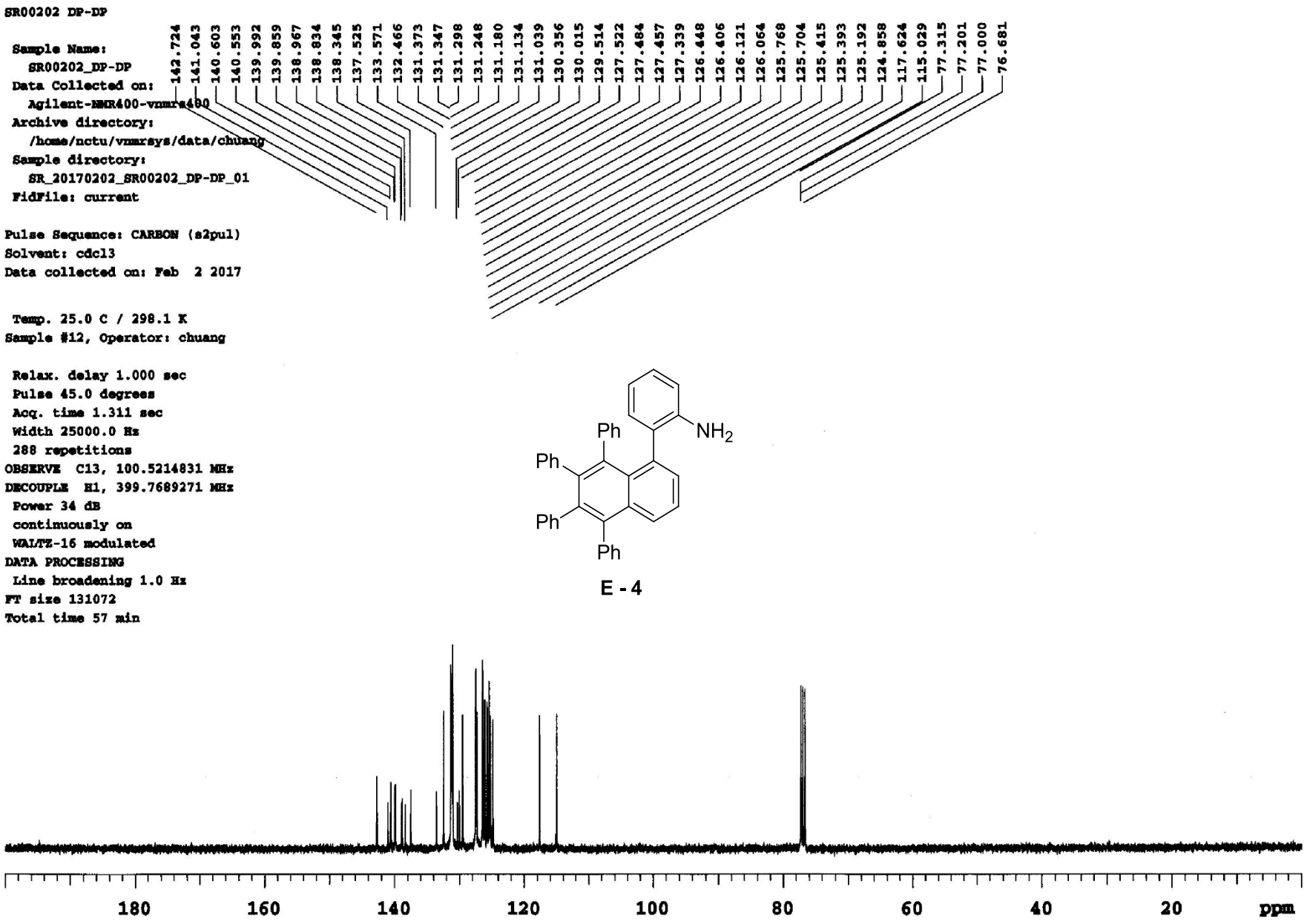


Figure S11. ^{1}H-NMR spectrum of compound **1f** ($CDCl_3$,400 MHz)

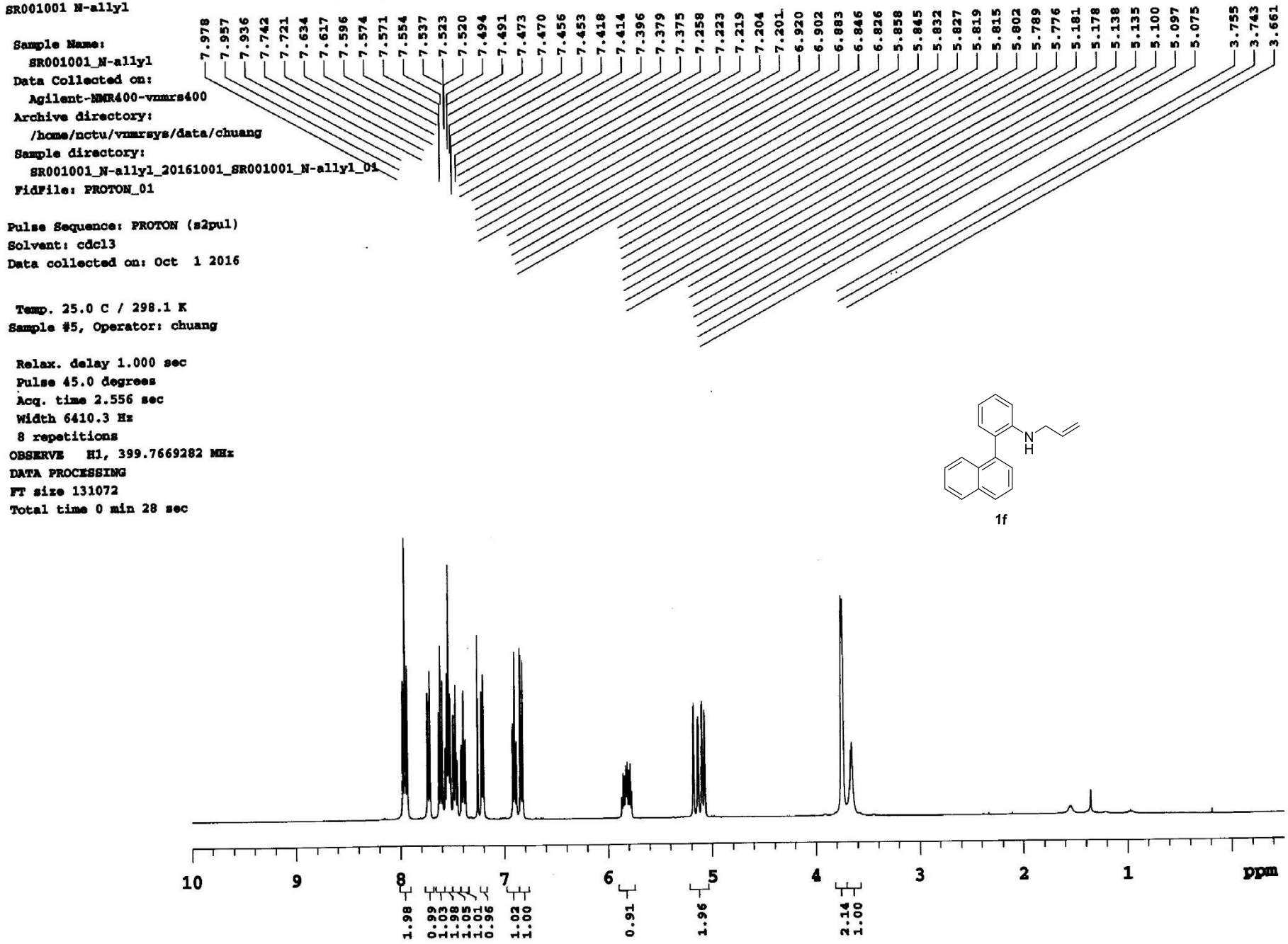


Figure S12. ^{13}C-NMR spectrum of compound **1f** ($CDCl_3$,100 MHz)

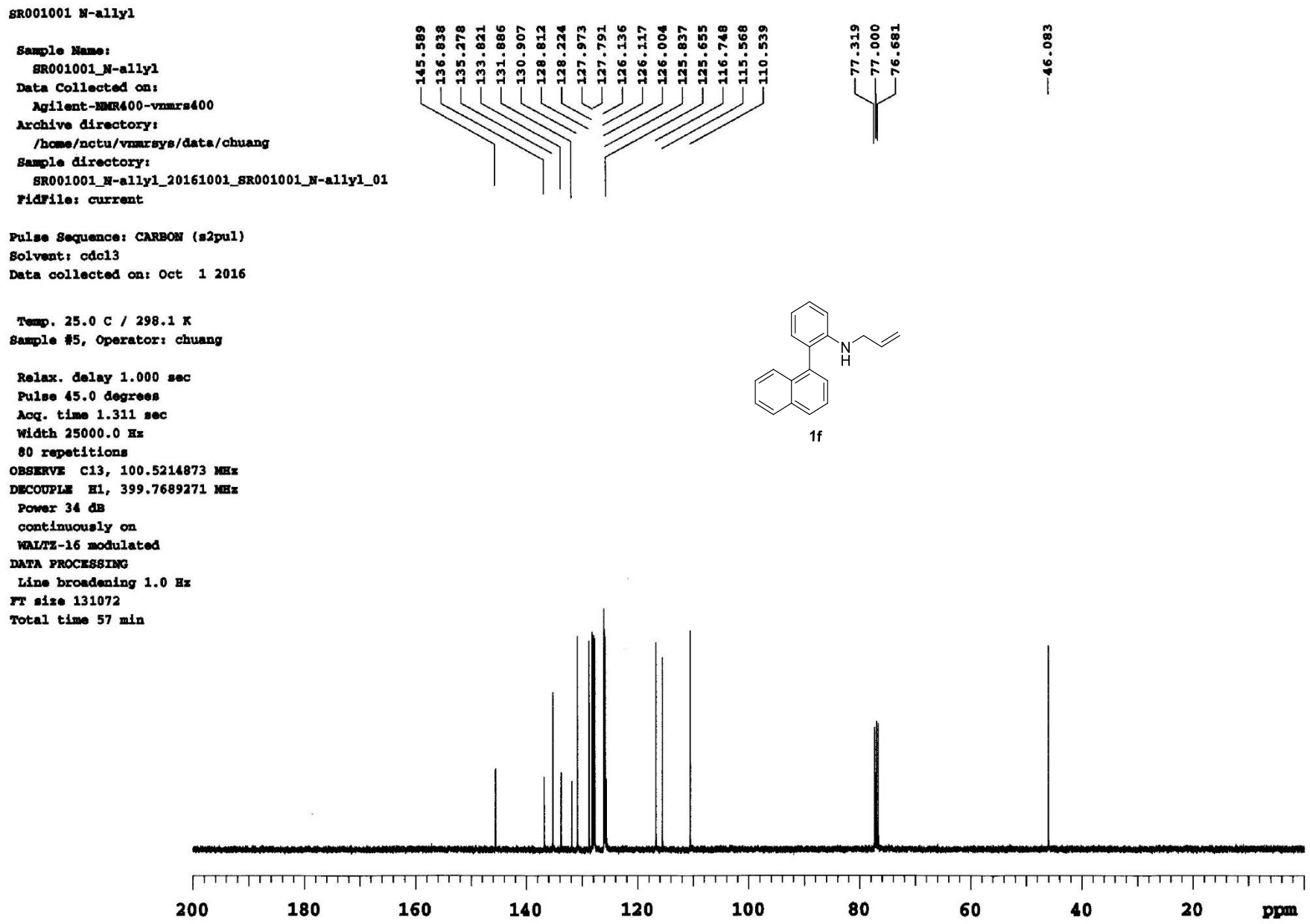


Figure S13. ^{1}H-NMR spectrum of compound **1g** ($CDCl_3$, 400 MHz)

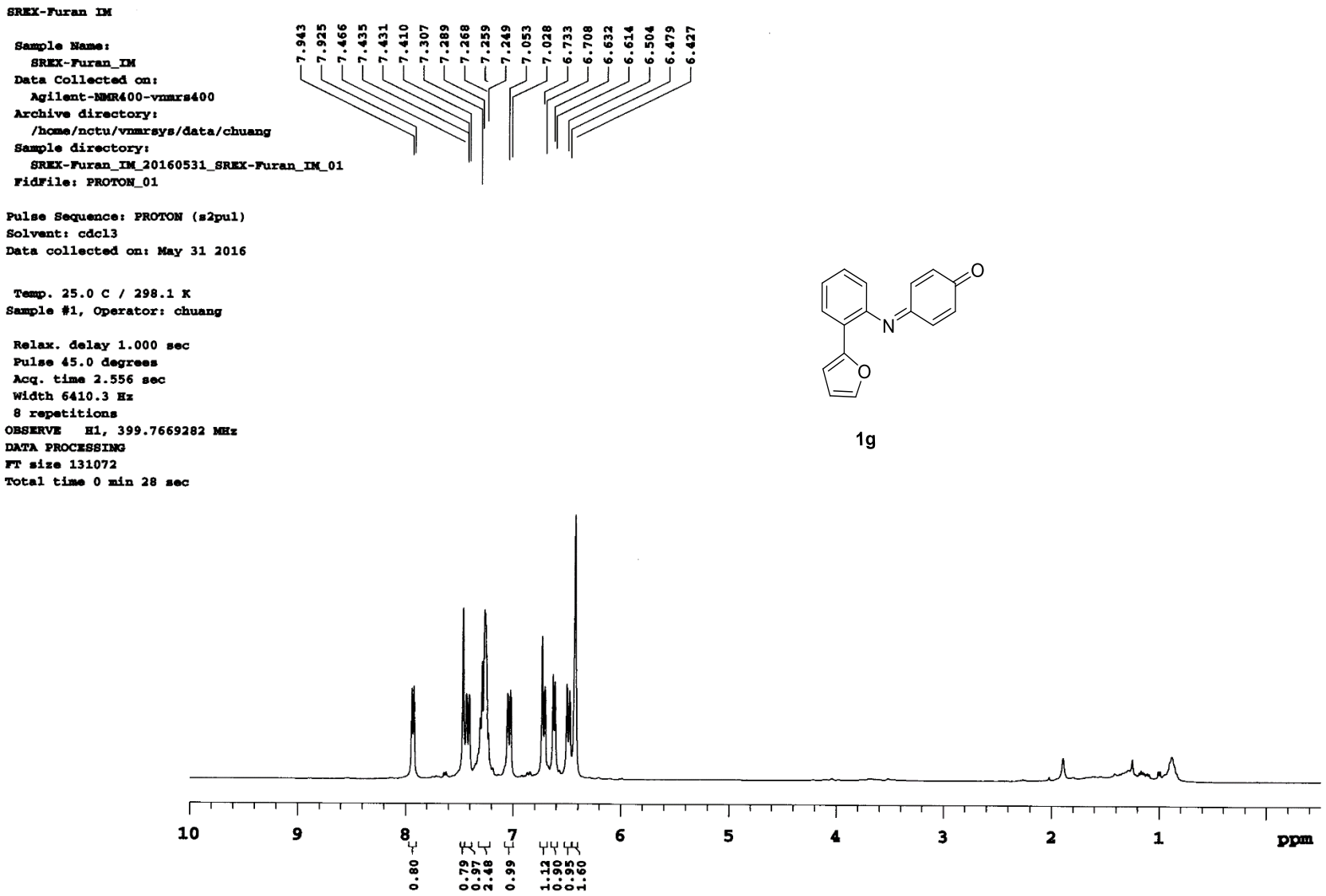


Figure S14. ^{13}C-NMR spectrum of compound **1g** ($CDCl_3$, 400 MHz)

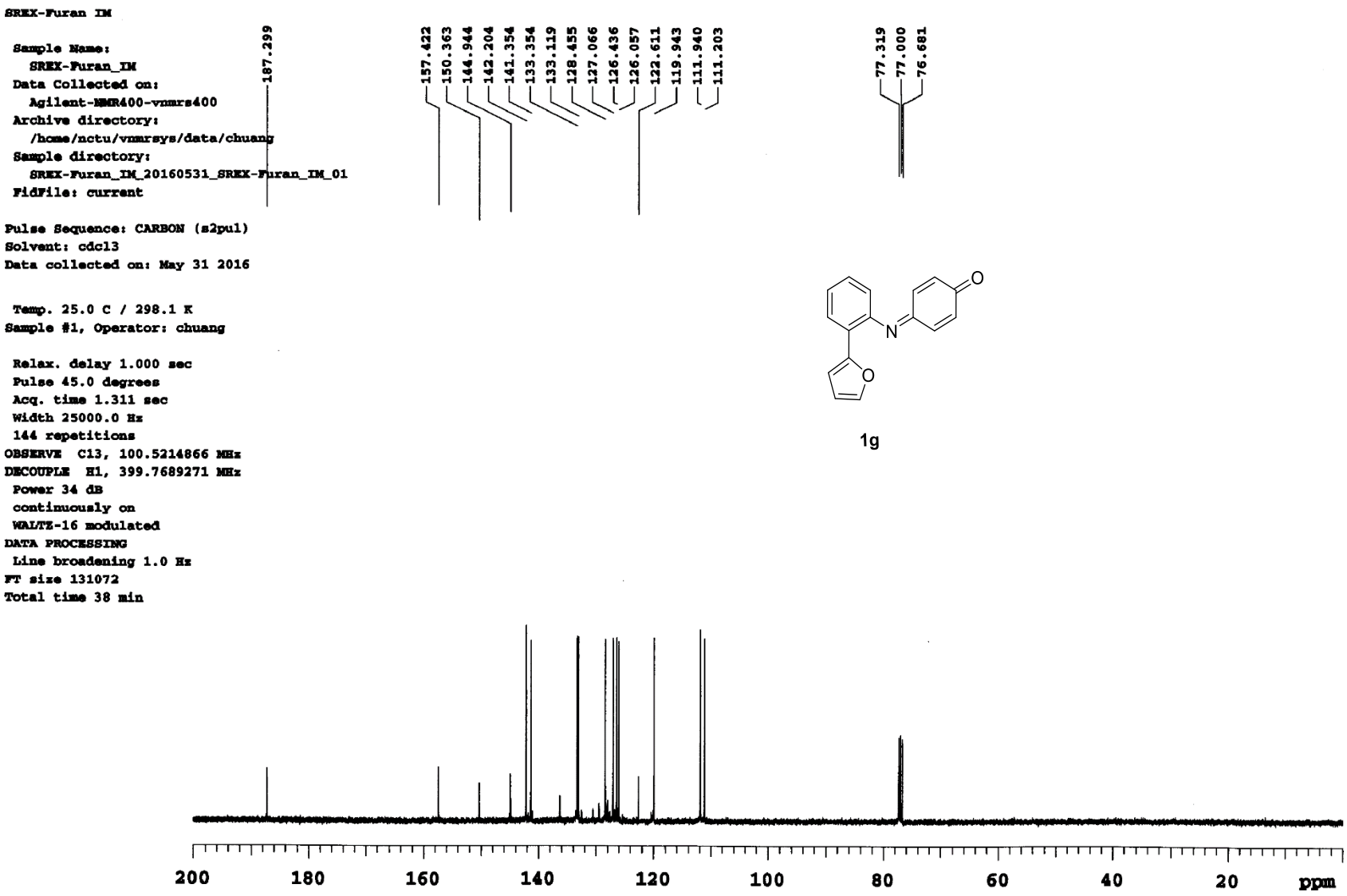


Figure S15. ^{1}H-NMR spectrum of compound **3a** ($CDCl_3$,400 MHz)

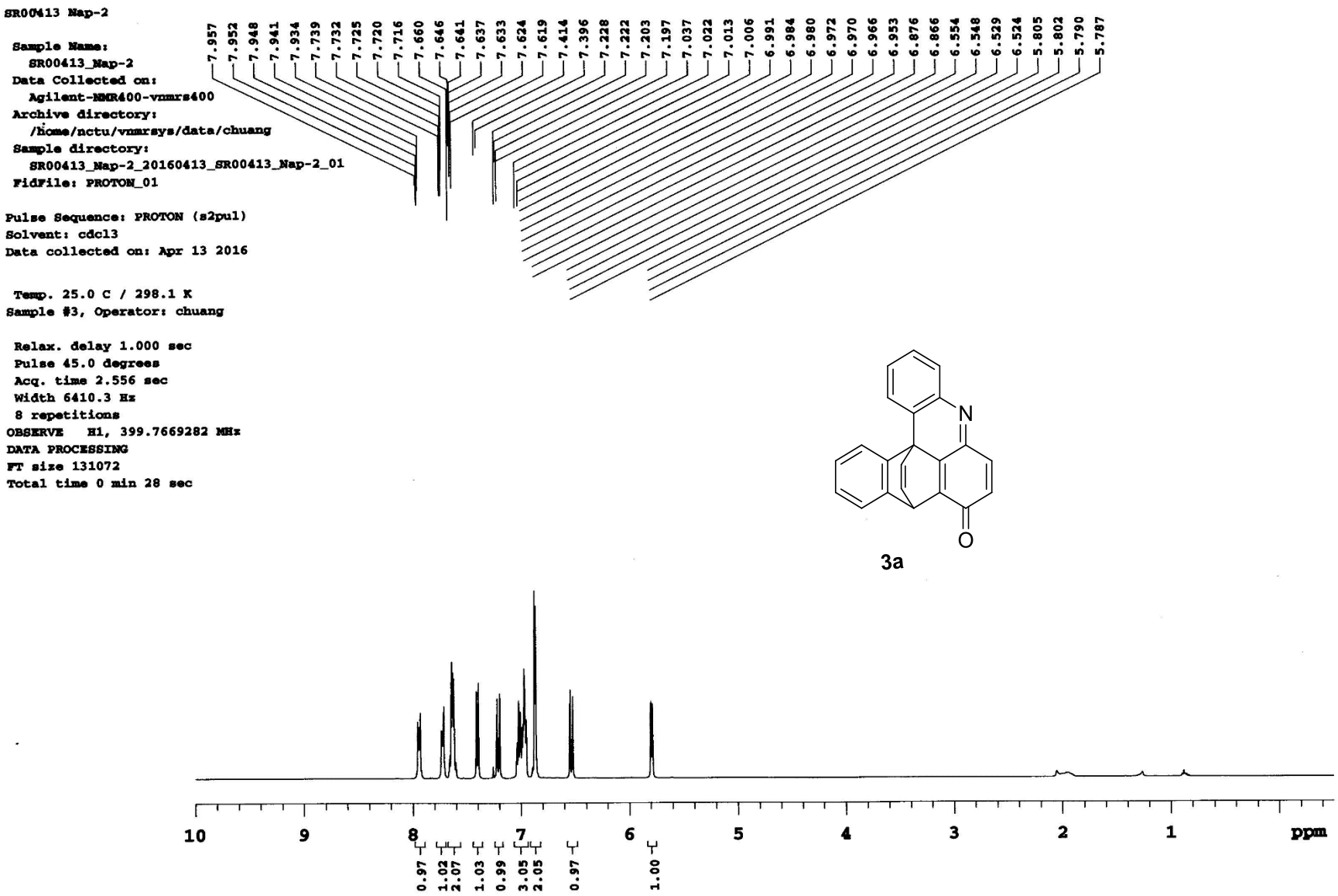


Figure S16. ^{13}C-NMR spectrum of compound **3a** ($CDCl_3$,100 MHz)

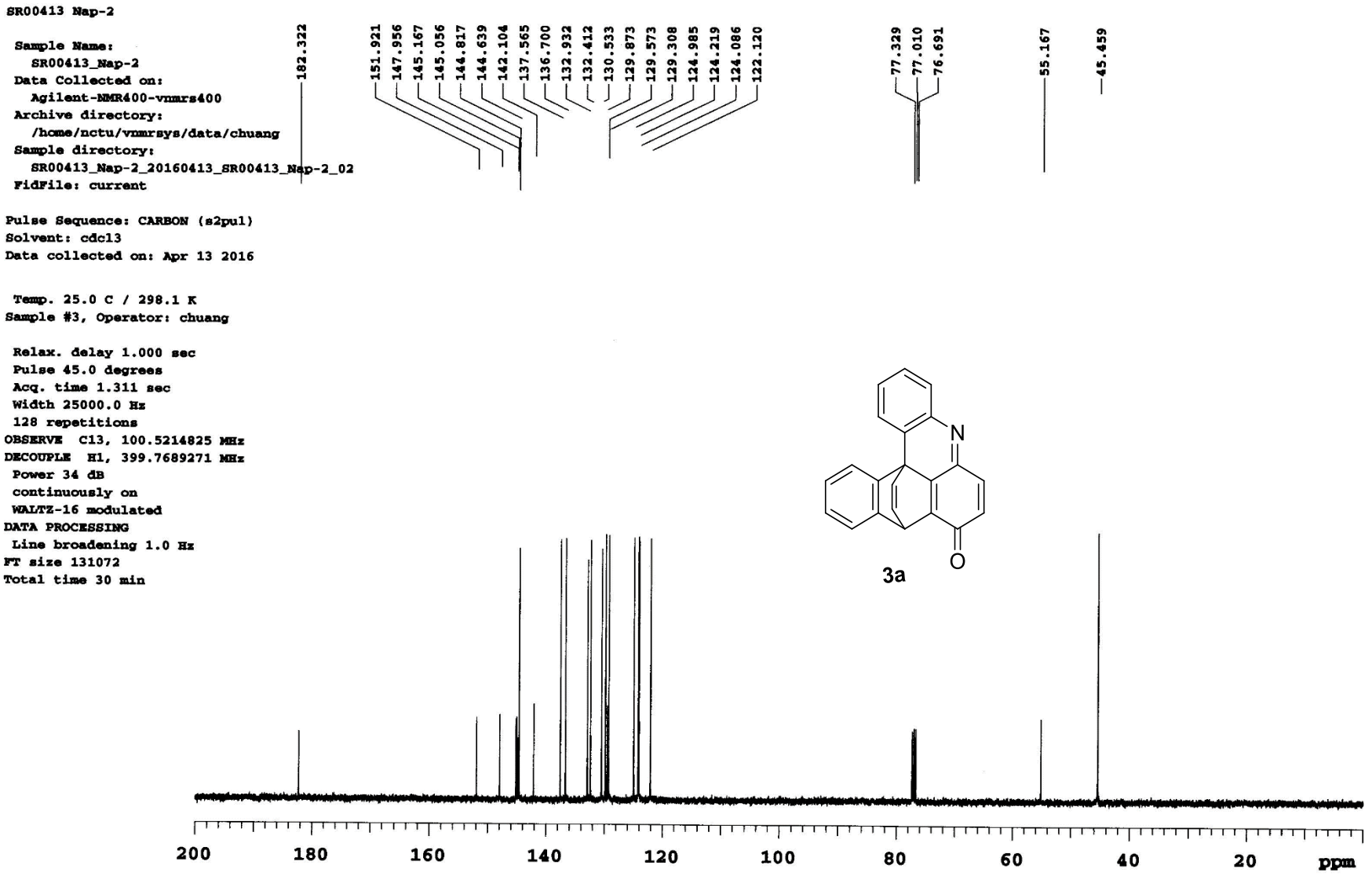


Figure S17. ^{1}H-NMR spectrum of compound **3b** ($CDCl_3$,400 MHz)

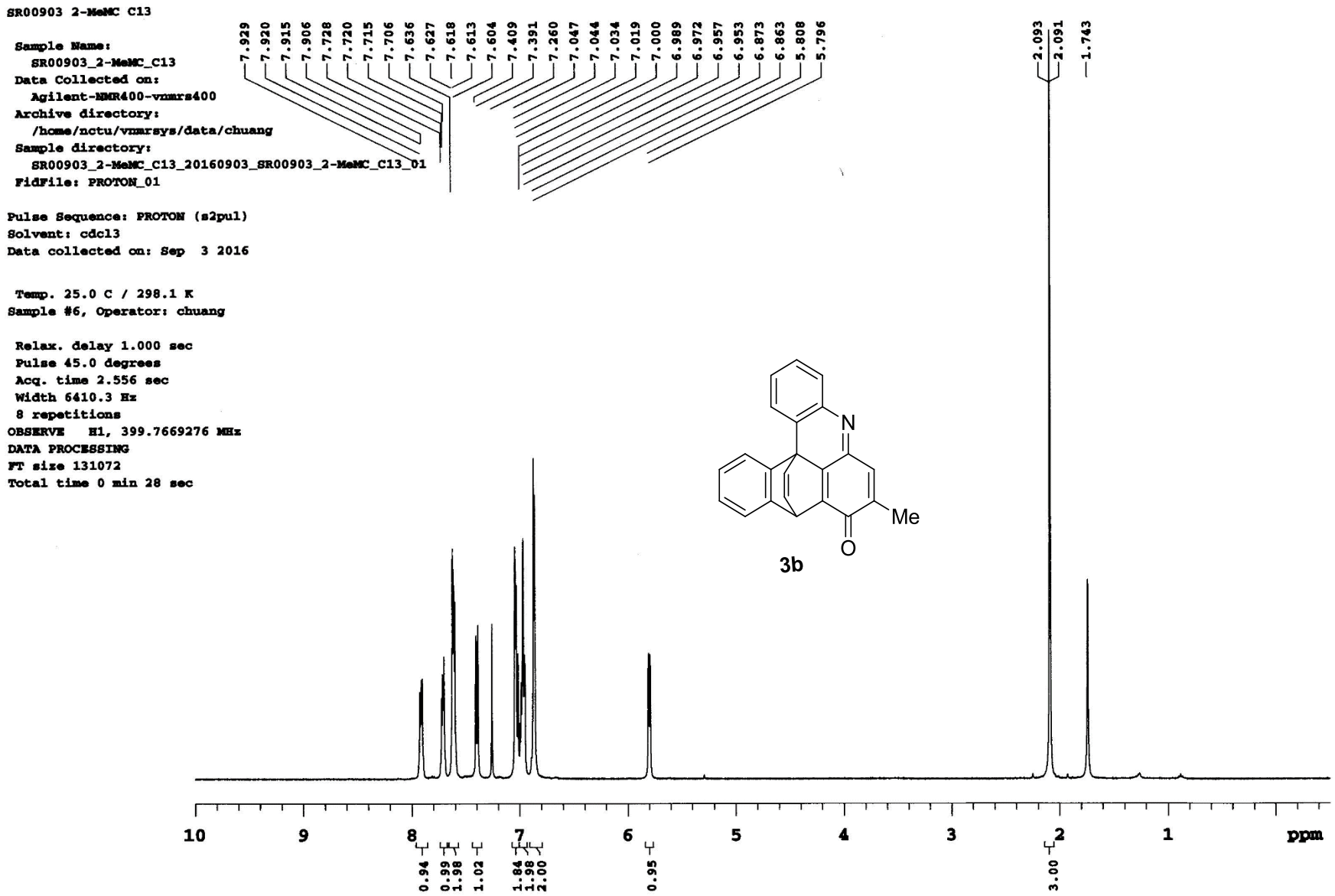


Figure S18. ^{13}C-NMR spectrum of compound **3b** ($CDCl_3$,100 MHz)

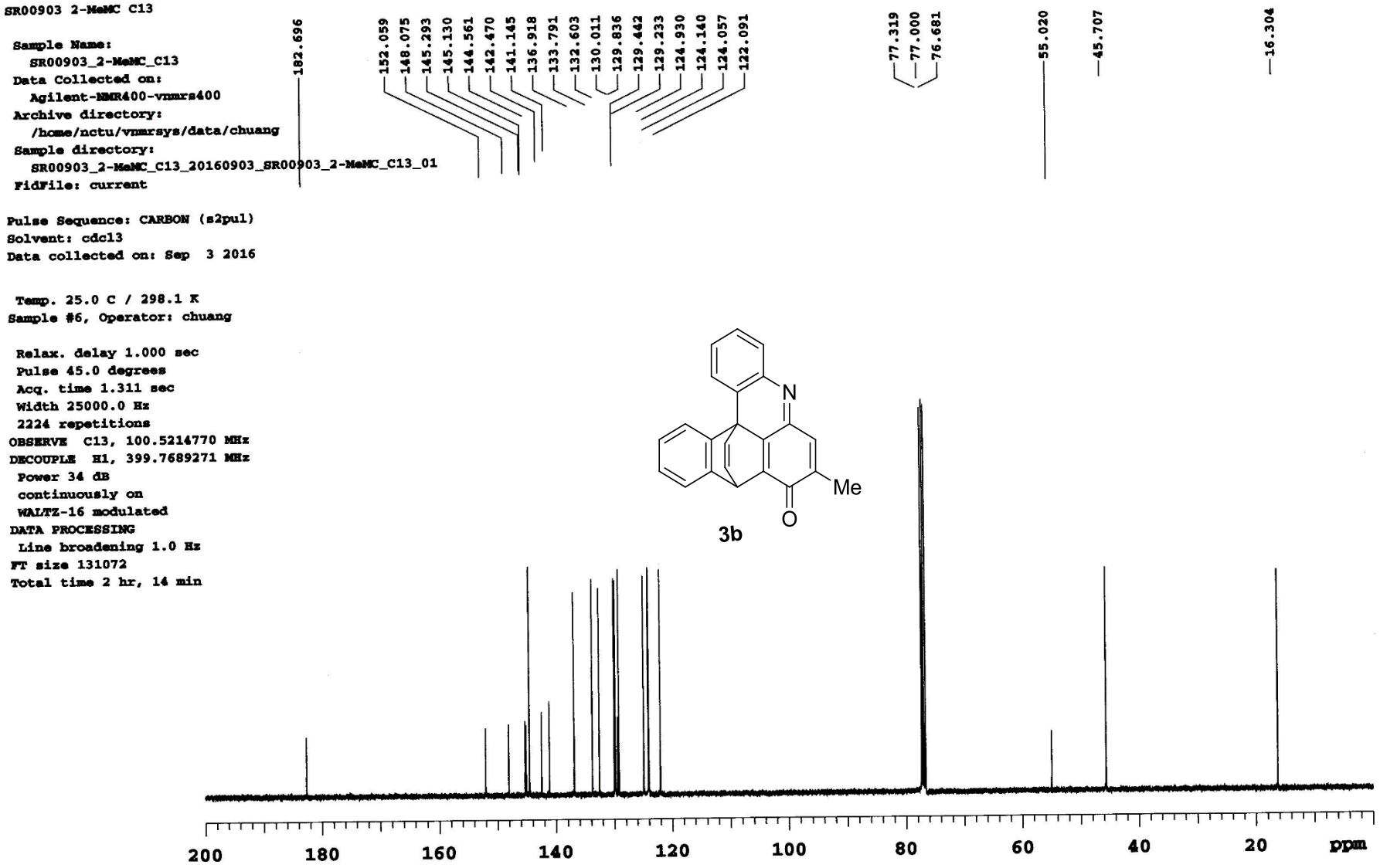


Figure S19. ^{1}H-NMR spectrum of compound **3c** ($CDCl_3$,400 MHz)

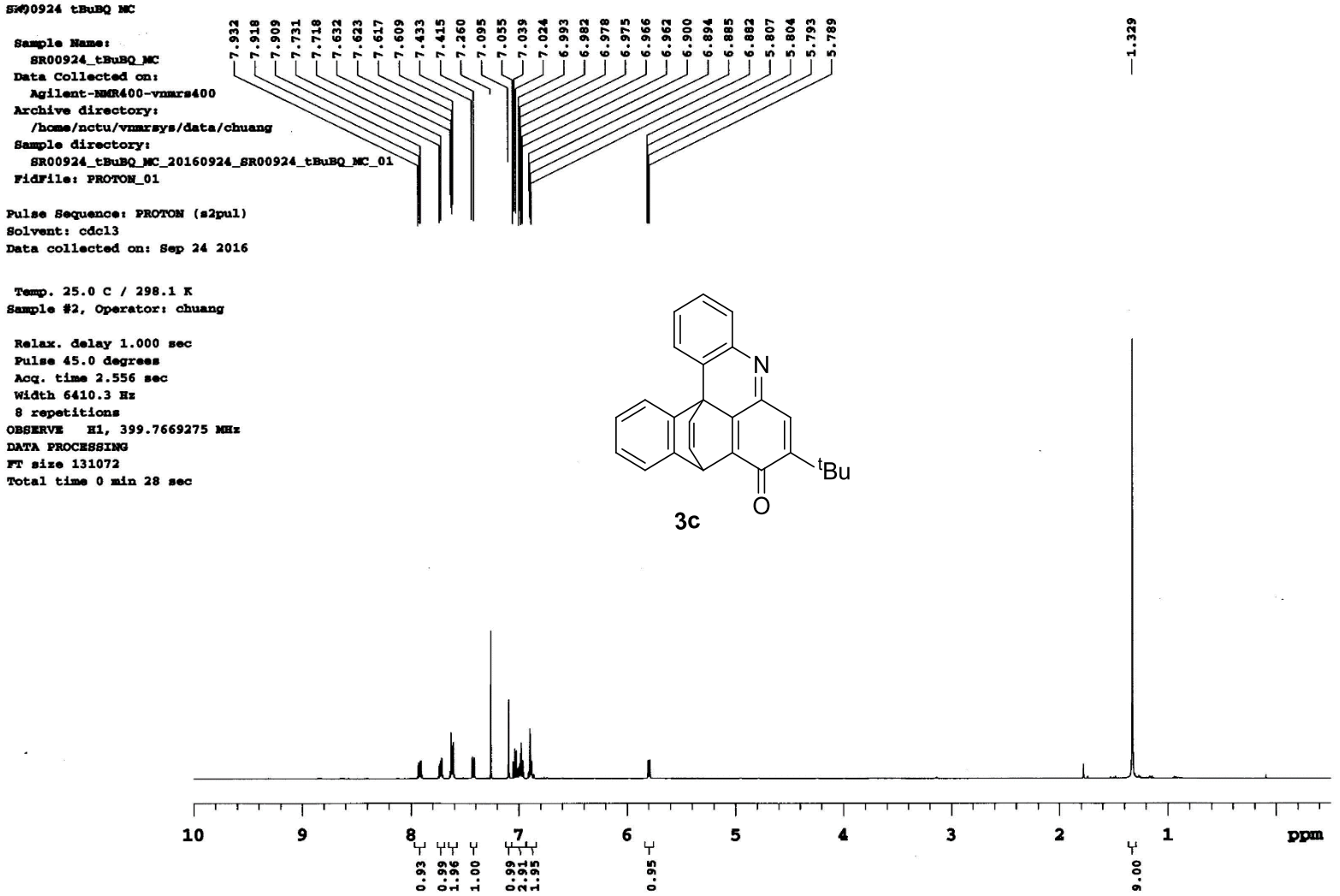


Figure S20. ^{1}H-NMR spectrum of compound **3c** ($CDCl_3$,100 MHz)

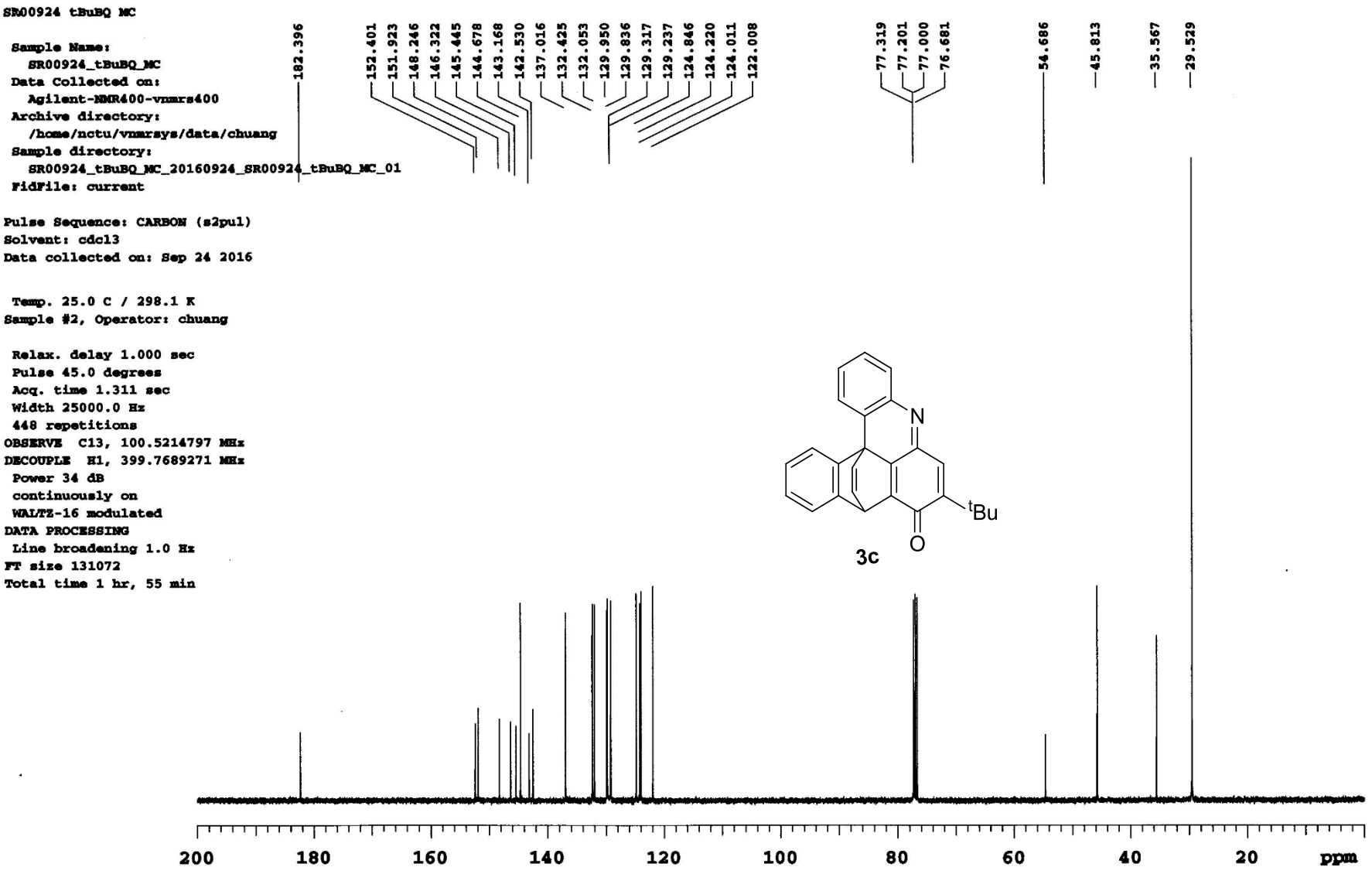


Figure S21. ^{1}H-NMR spectrum of compound **3d** ($CDCl_3$,400 MHz)

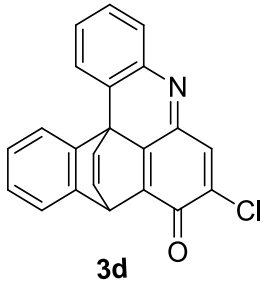
```
SR001026 2clBQ

 Sample Name:
   SR001026_2clBQ
 Data Collected on:
   Agilent-NMR400-vnmrs400
 Archive directory:
   /home/nctu/vnmrsys/data/chuang
 Sample directory:
   SR001026_2clBQ_20161026_SR001026_2clBQ_01
 FidFile: PROTON_01

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Oct 26 2016


 Temp. 25.0 C / 298.1 K
Sample #6, Operator: chuang

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 2.556 sec
 Width 6410.3 Hz
 8 repetitions
OBSERVE   H1, 399.7669282 MHz
DATA PROCESSING
FT size 131072
Total time 0 min 28 sec
```



3d

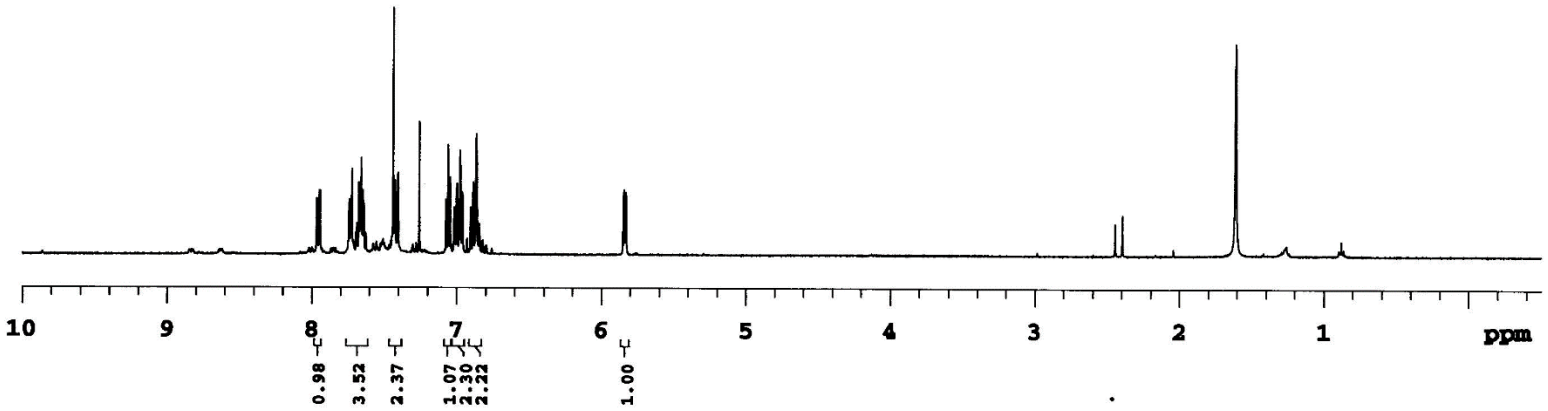


Figure S22. ^{13}C-NMR spectrum of compound **3d** ($CDCl_3$,100 MHz)

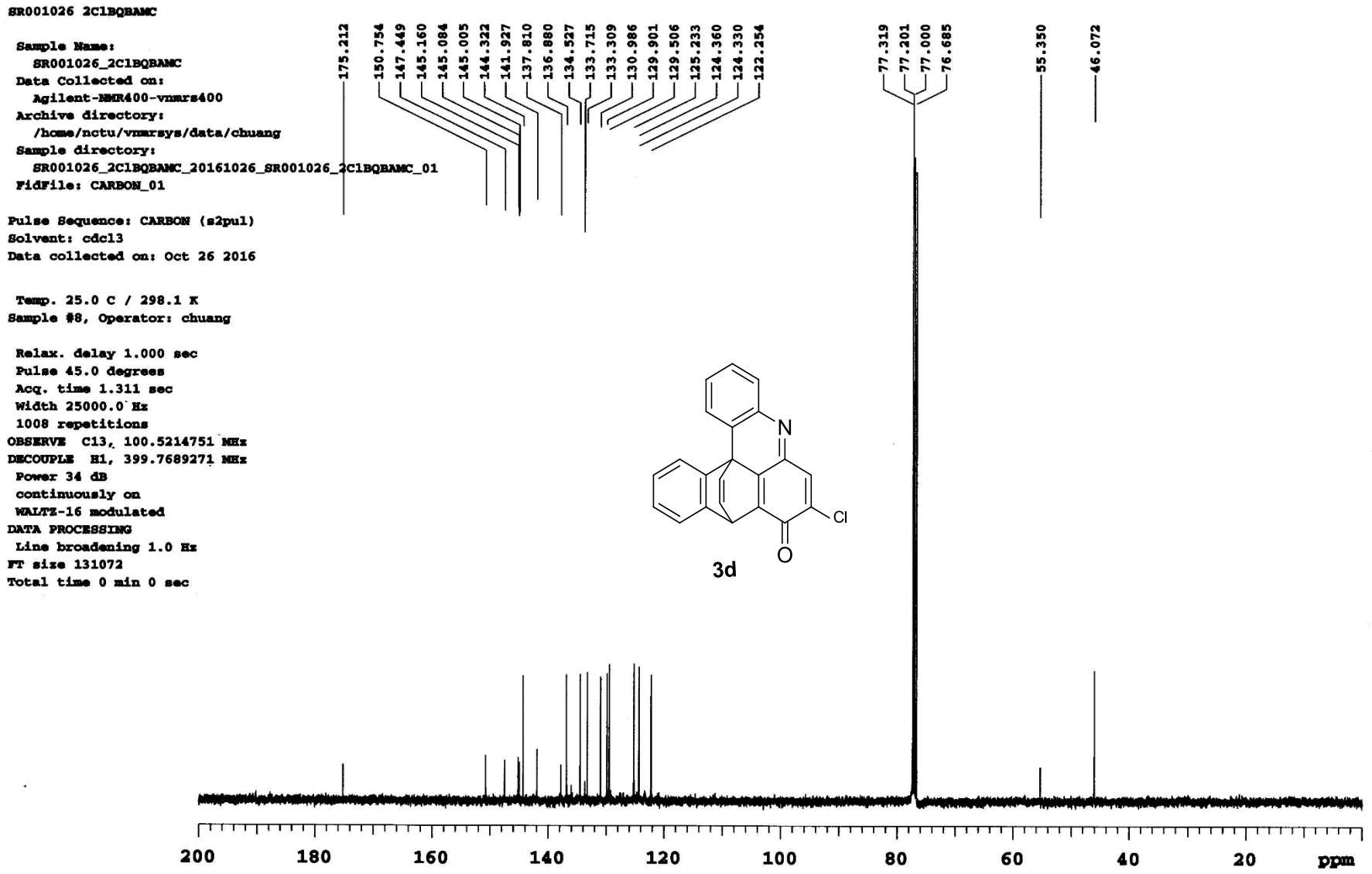


Figure S23. ^{1}H-NMR spectrum of compound **3e** ($CDCl_3$,400 MHz)

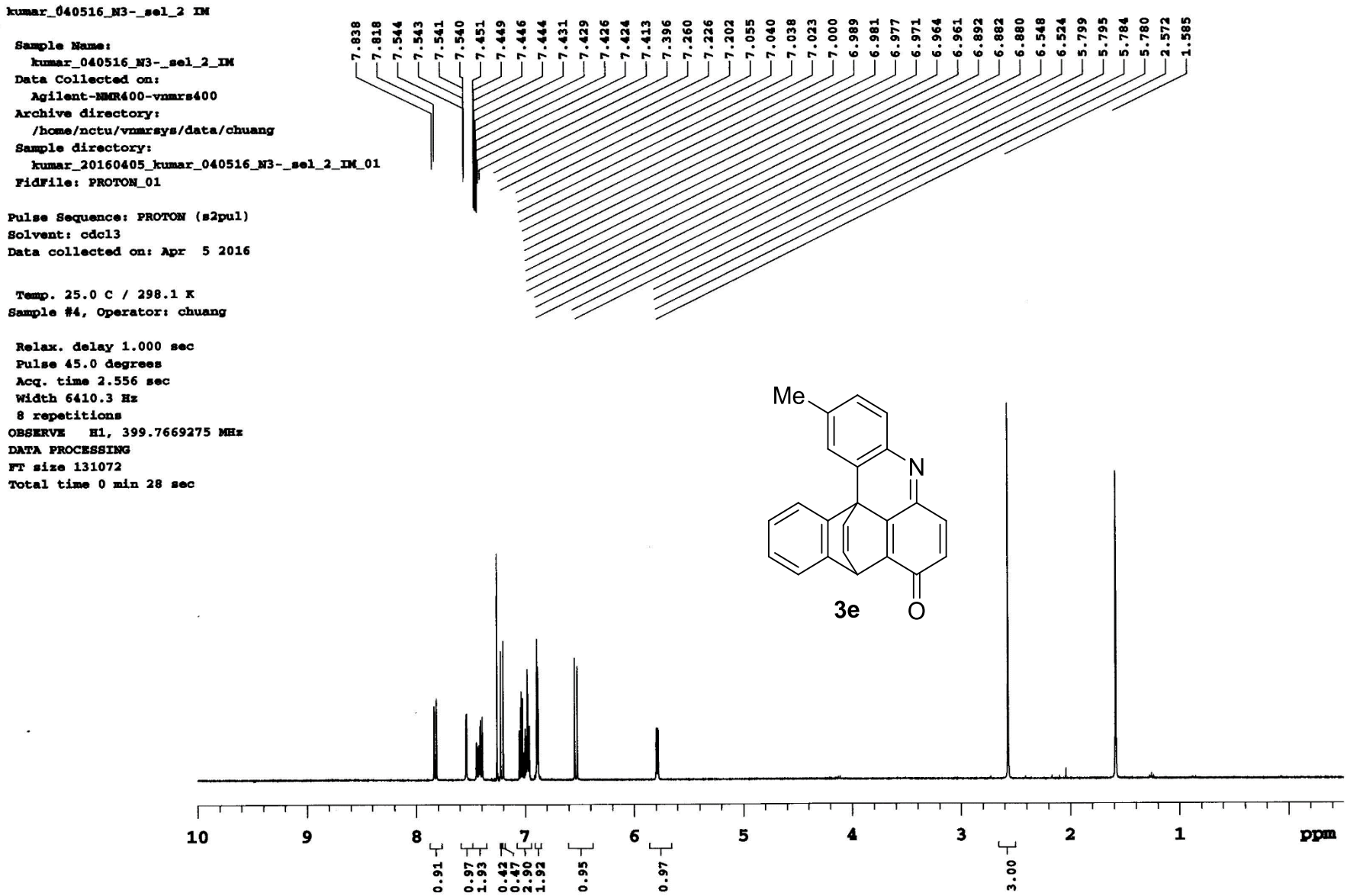


Figure S24. ^{13}C-NMR spectrum of compound **3e** ($CDCl_3$,100 MHz)

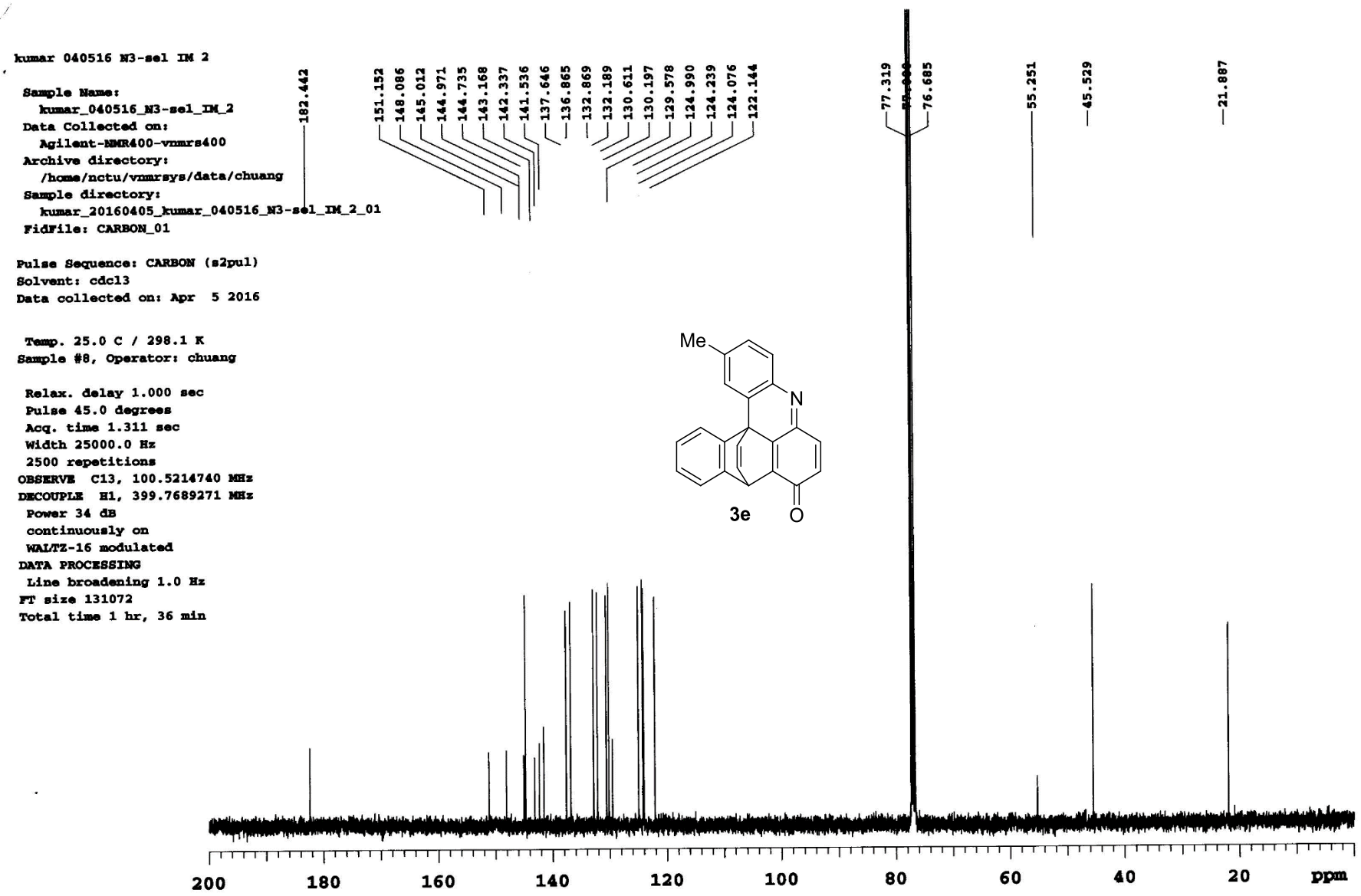


Figure S25. ^{1}H-NMR spectrum of compound **3f** ($CDCl_3$,400 MHz)

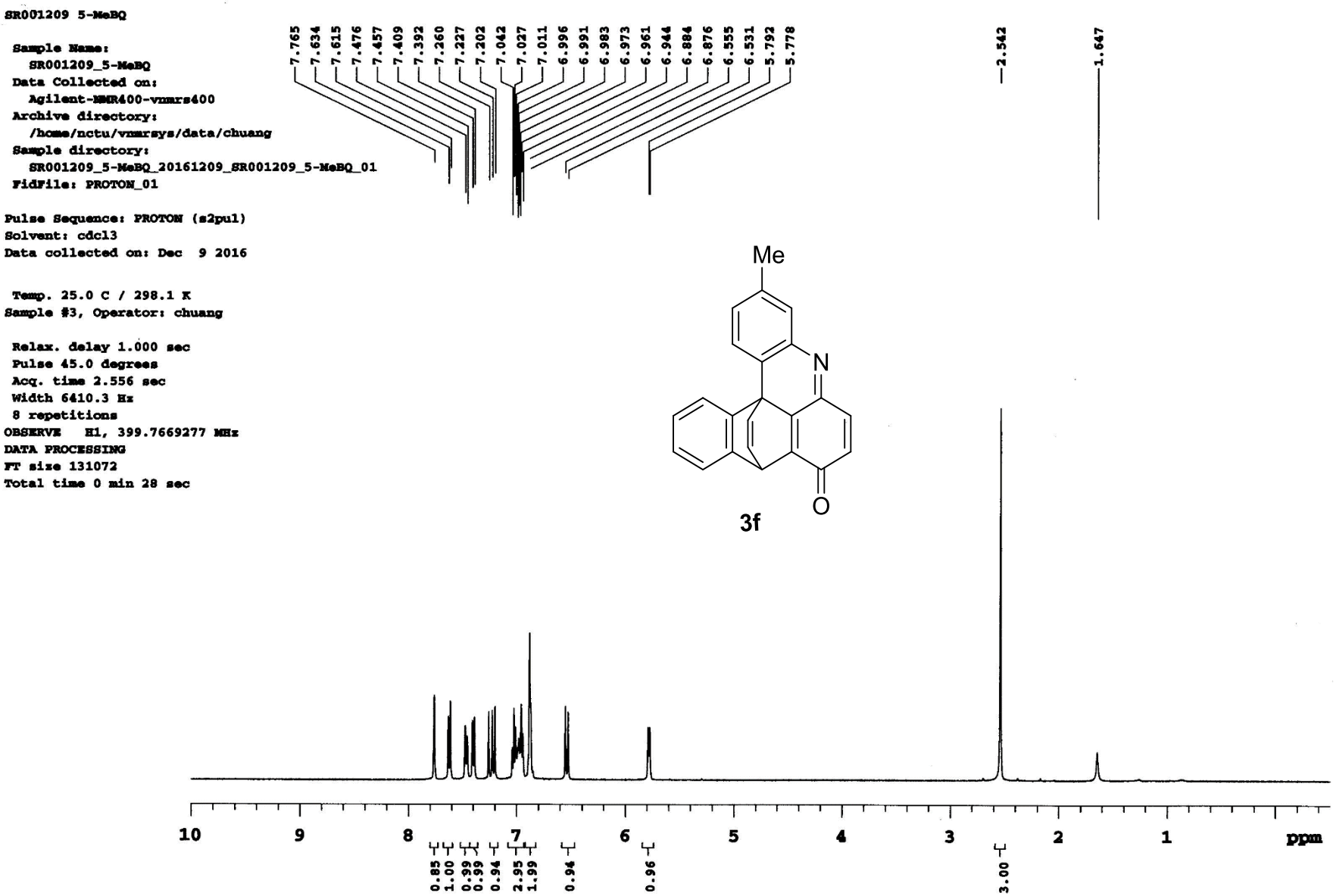


Figure S26. ^{13}C-NMR spectrum of compound **3f** ($CDCl_3$,100 MHz)

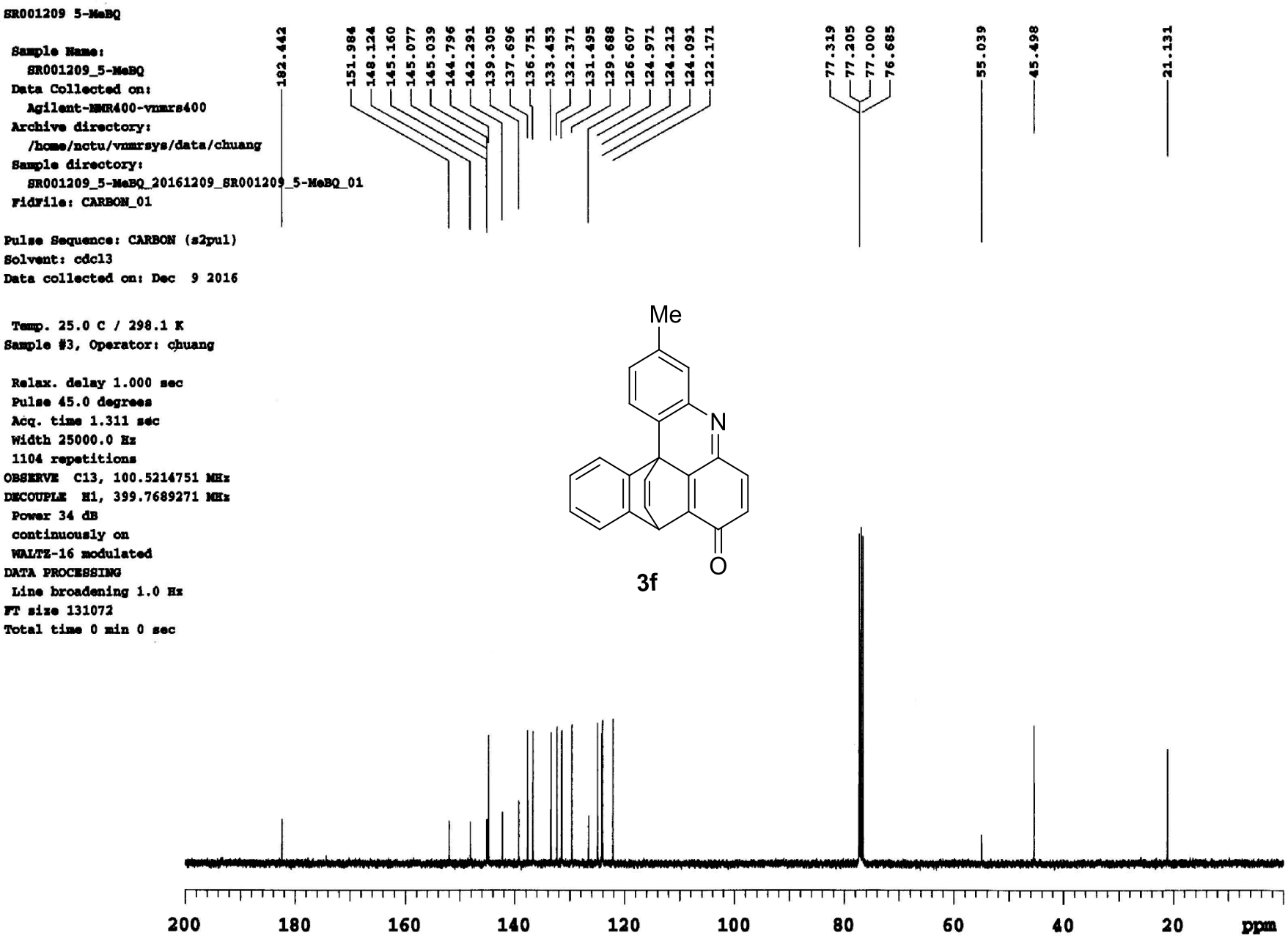


Figure S27. ^{1}H-NMR spectrum of compound **3g** ($CDCl_3$,400 MHz)

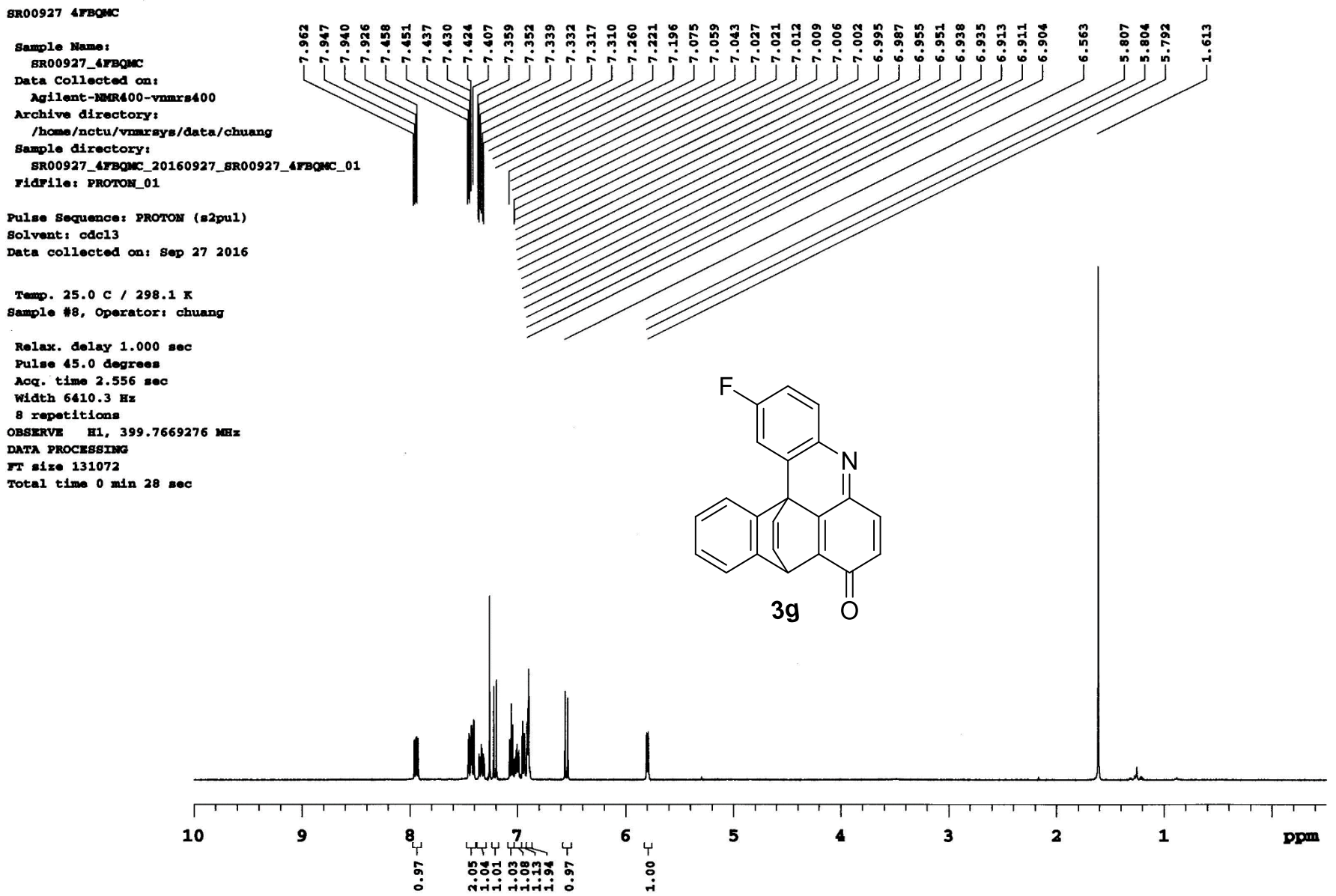


Figure S28. ^{13}C-NMR spectrum of compound **3g** ($CDCl_3$,100 MHz)

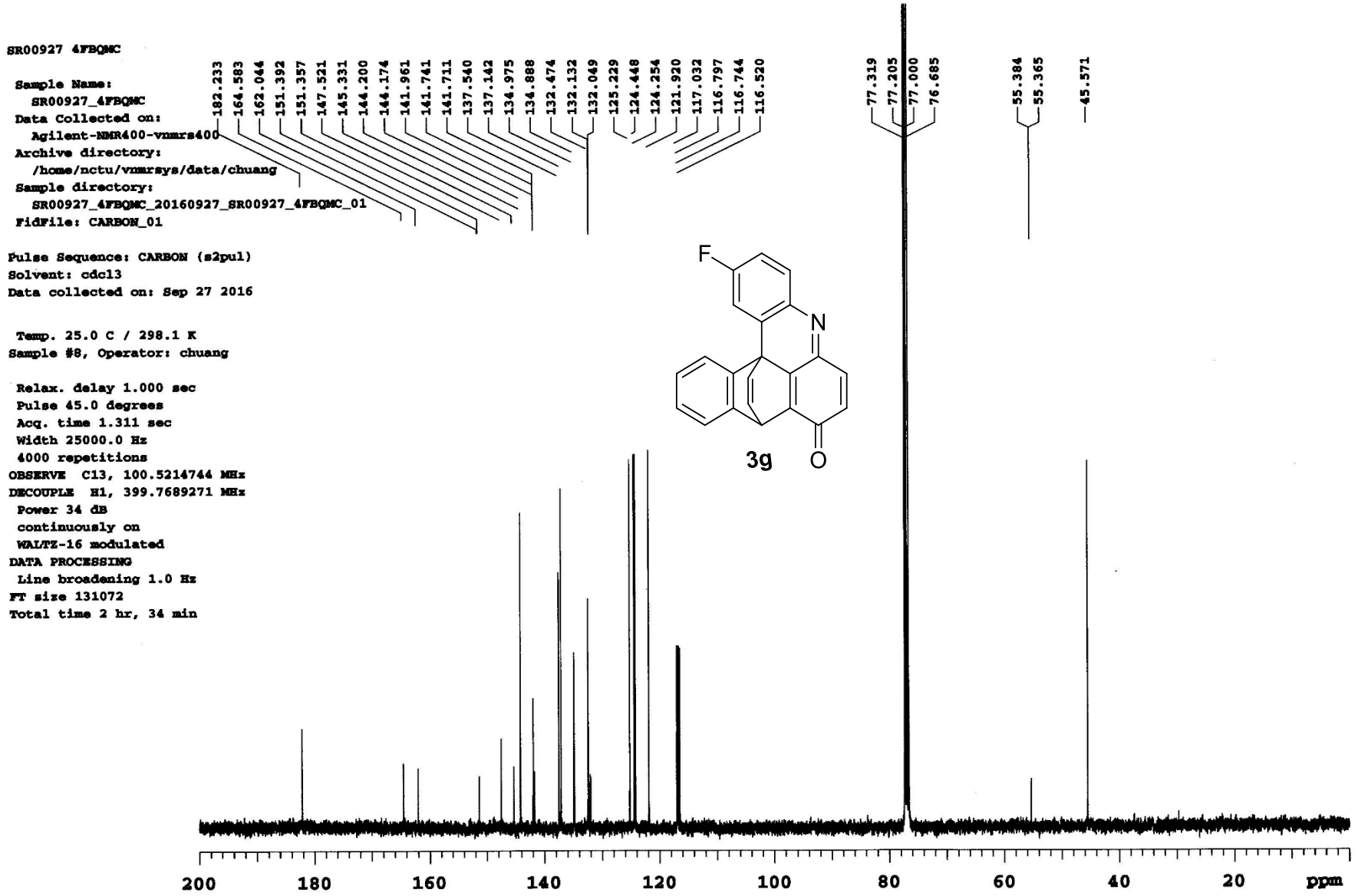


Figure S29. ^{1}H-NMR spectrum of compound **3h** ($CDCl_3$,400 MHz)

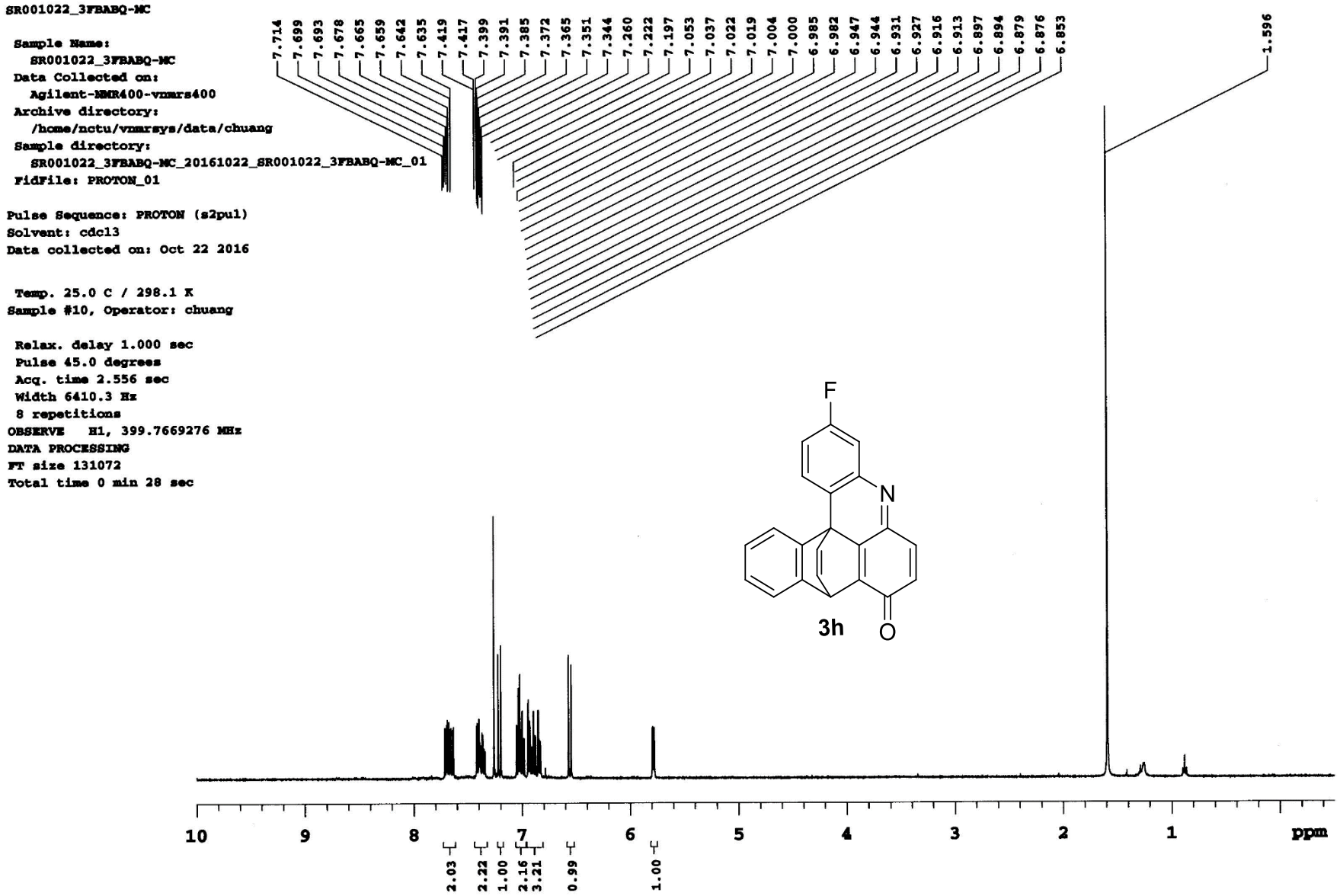


Figure S30. ^{13}C-NMR spectrum of compound **3h** ($CDCl_3$,100 MHz)

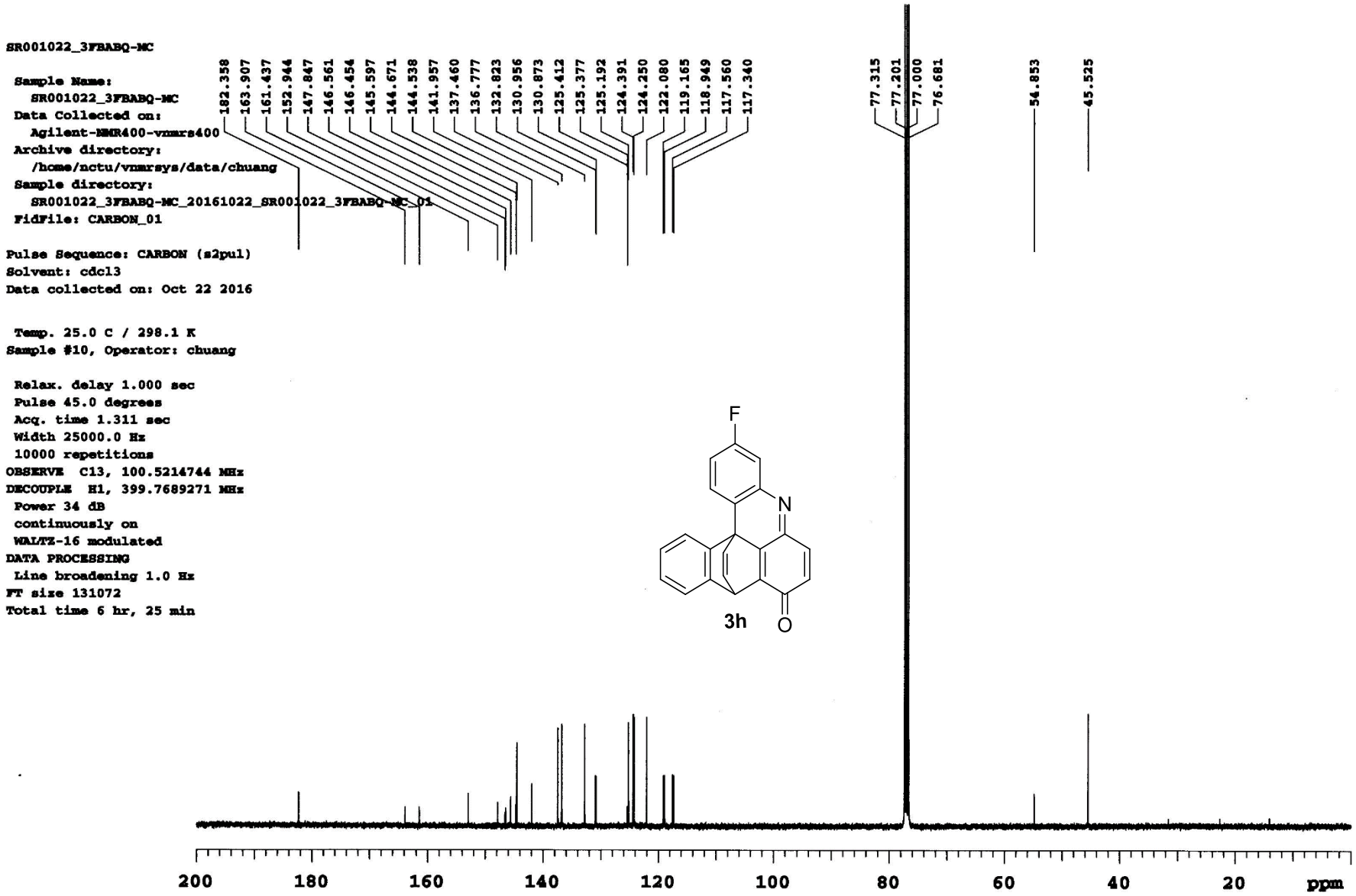


Figure S31. ^{1}H-NMR spectrum of compound **3i** ($CDCl_3$,400 MHz)

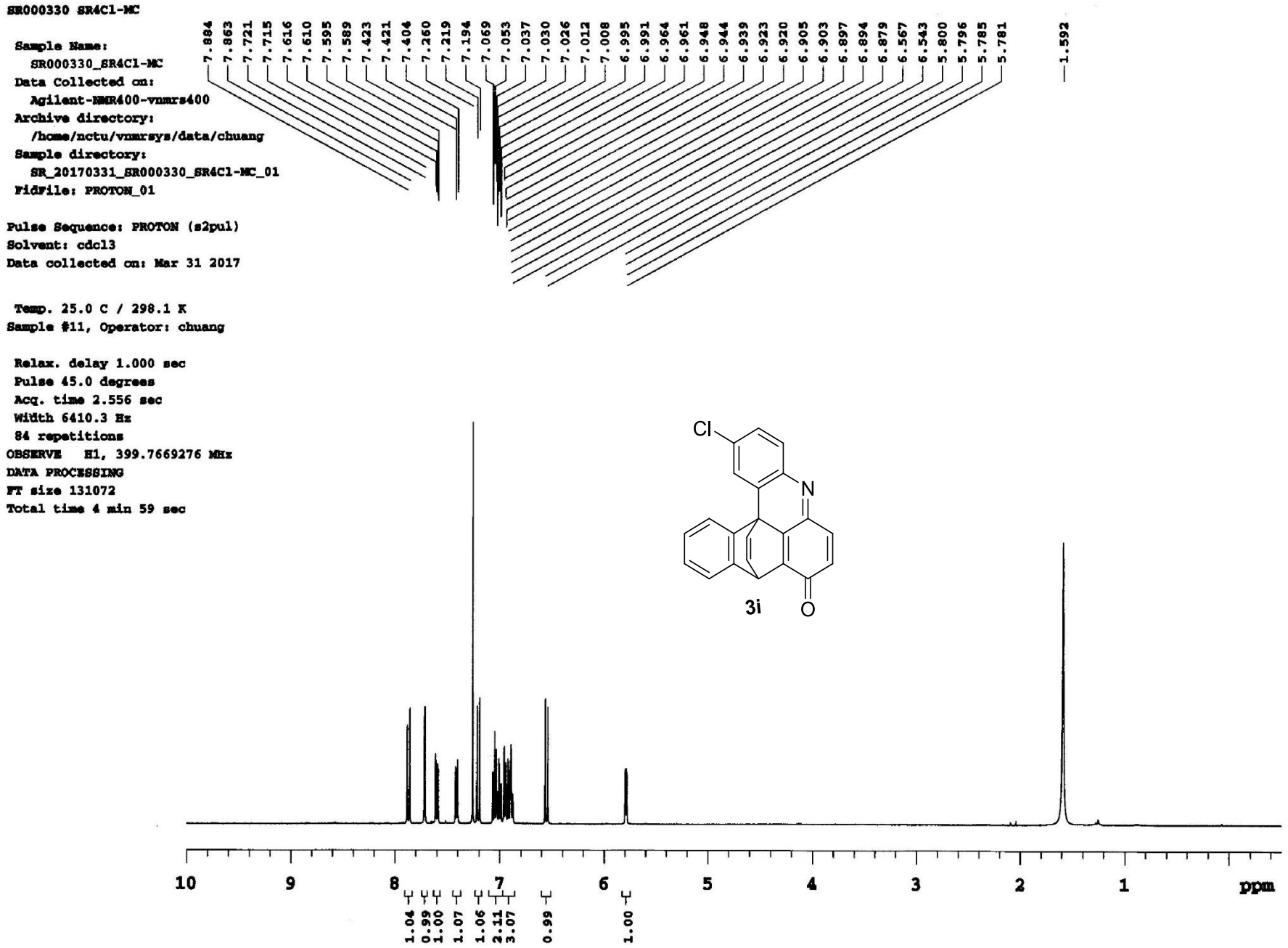


Figure S32. ^{13}C-NMR spectrum of compound **3i** ($CDCl_3$,400 MHz)

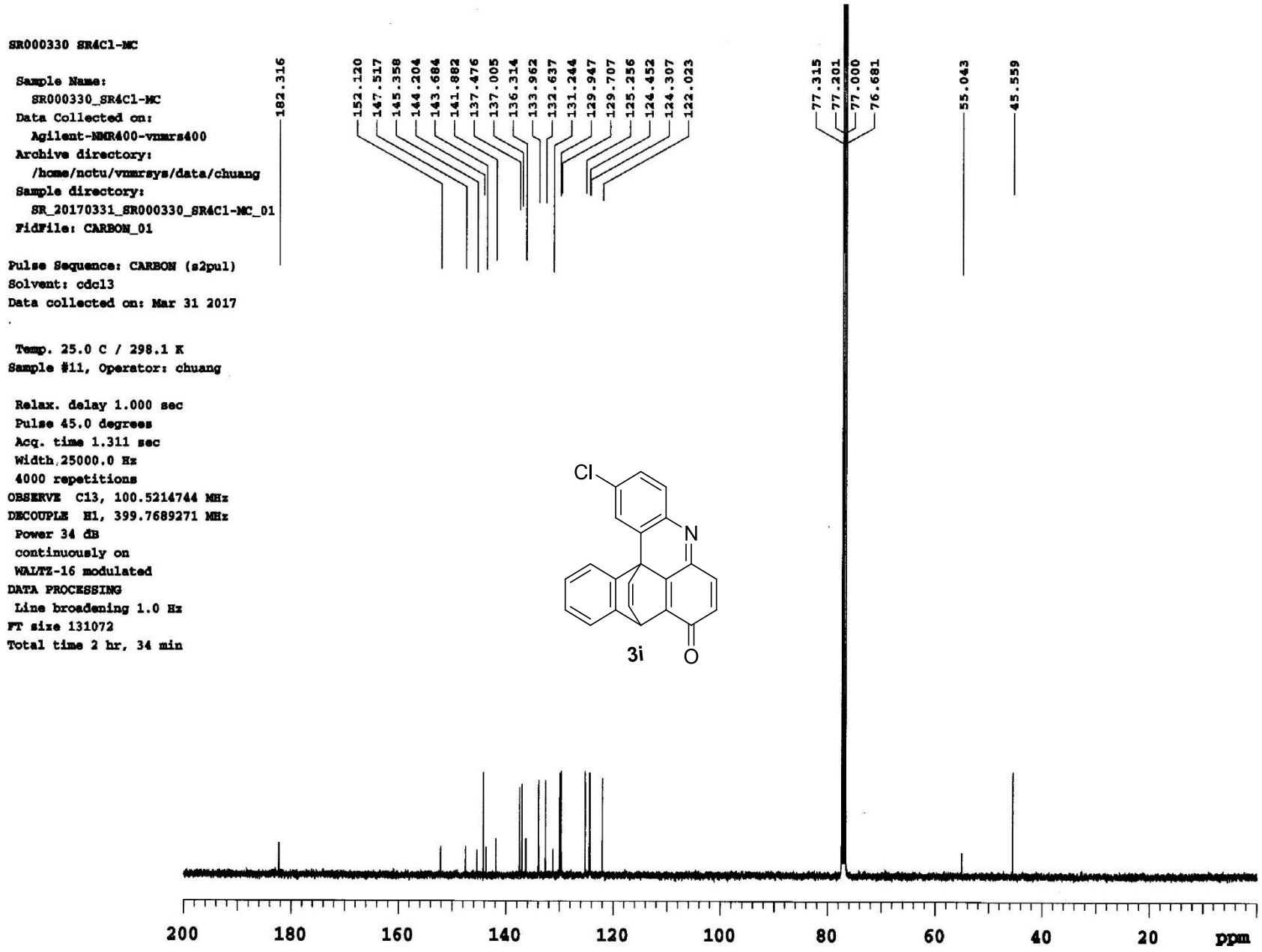


Figure S33. ^{1}H-NMR spectrum of compound **3j** ($CDCl_3$,400 MHz)

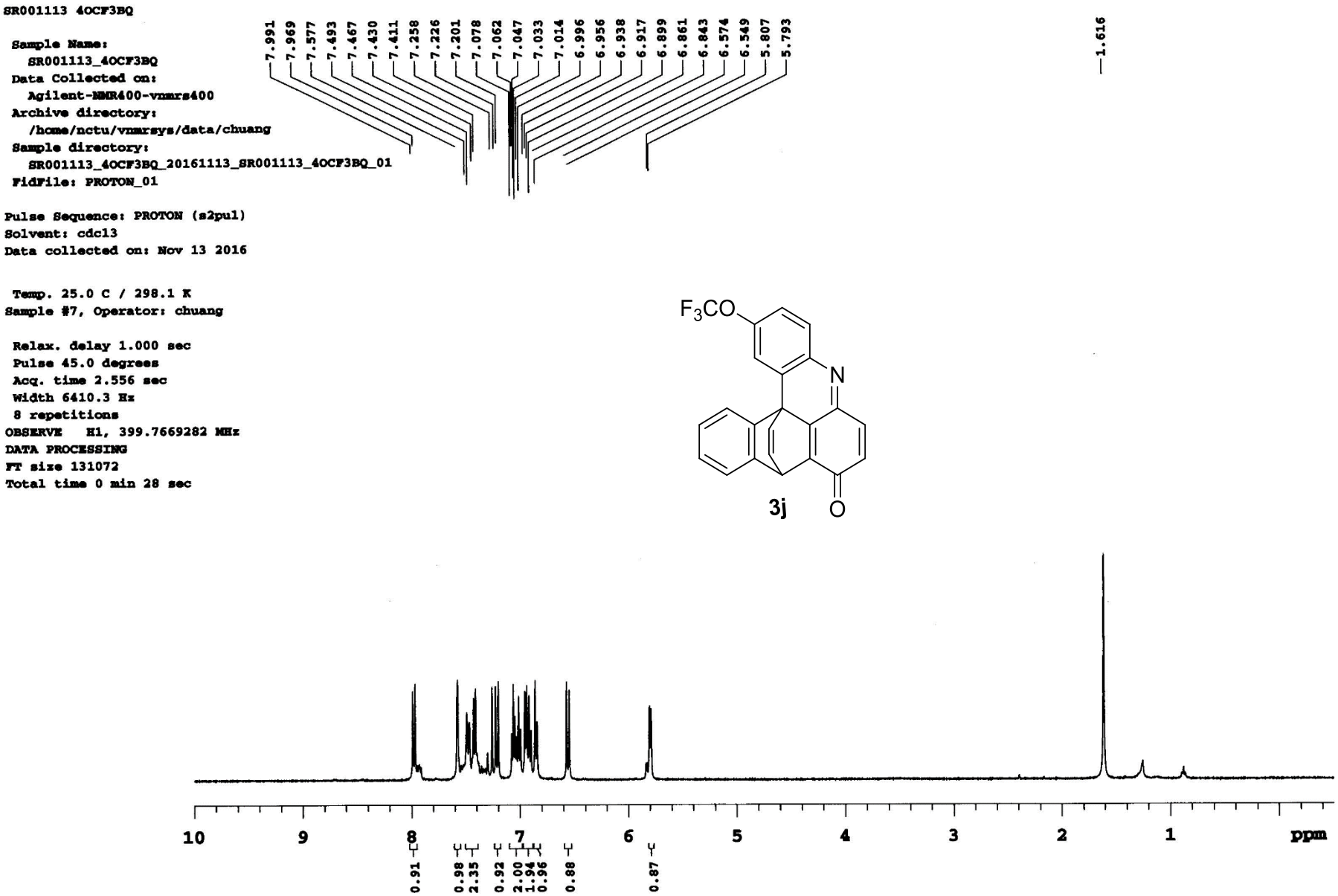


Figure S34. ^{13}C-NMR spectrum of compound **3j** ($CDCl_3$,100 MHz)

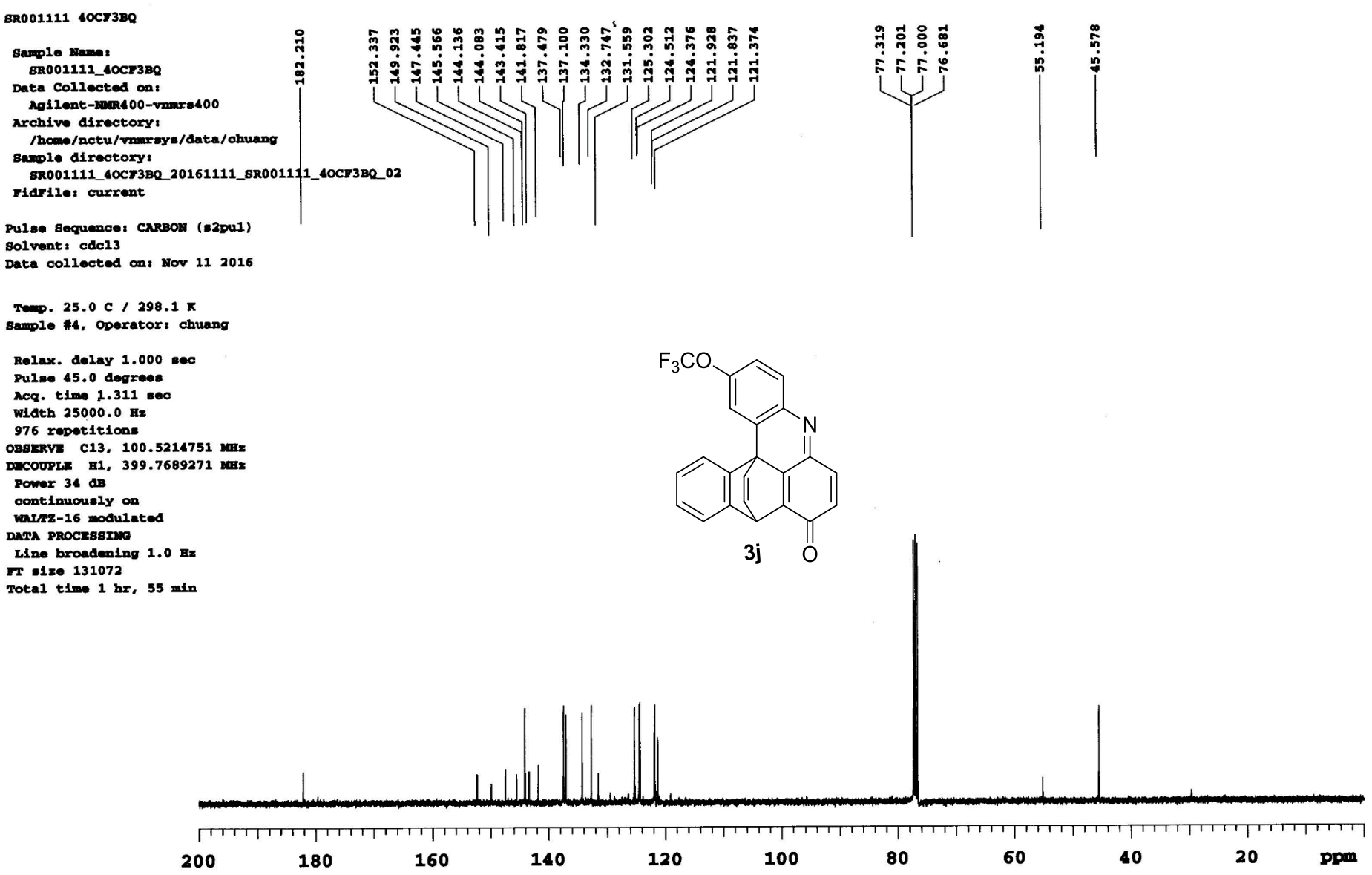


Figure S35. ^{1}H-NMR spectrum of compound **3k** ($CDCl_3$,400 MHz)

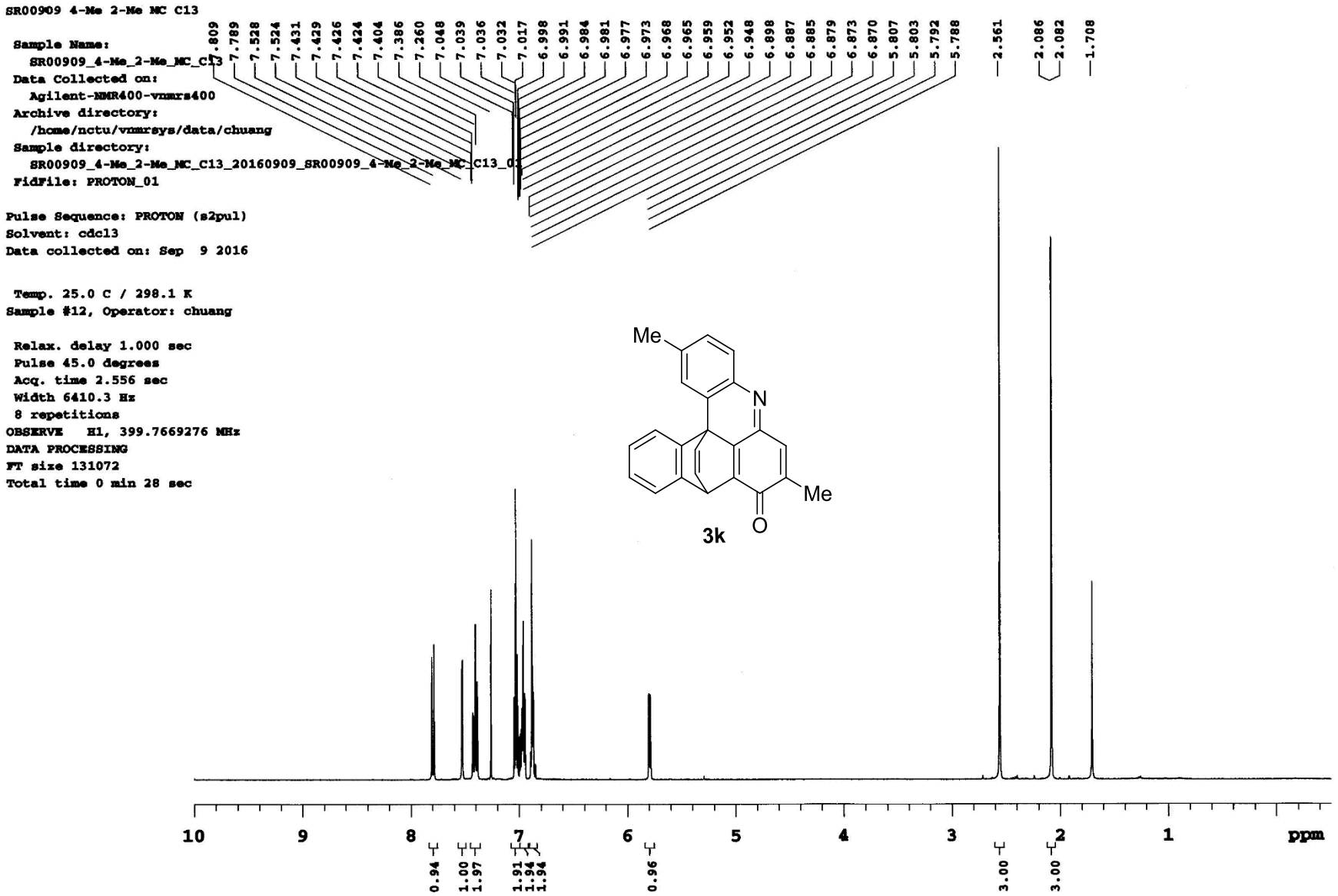


Figure S36. ^{13}C-NMR spectrum of compound **3k** ($CDCl_3$,100 MHz)

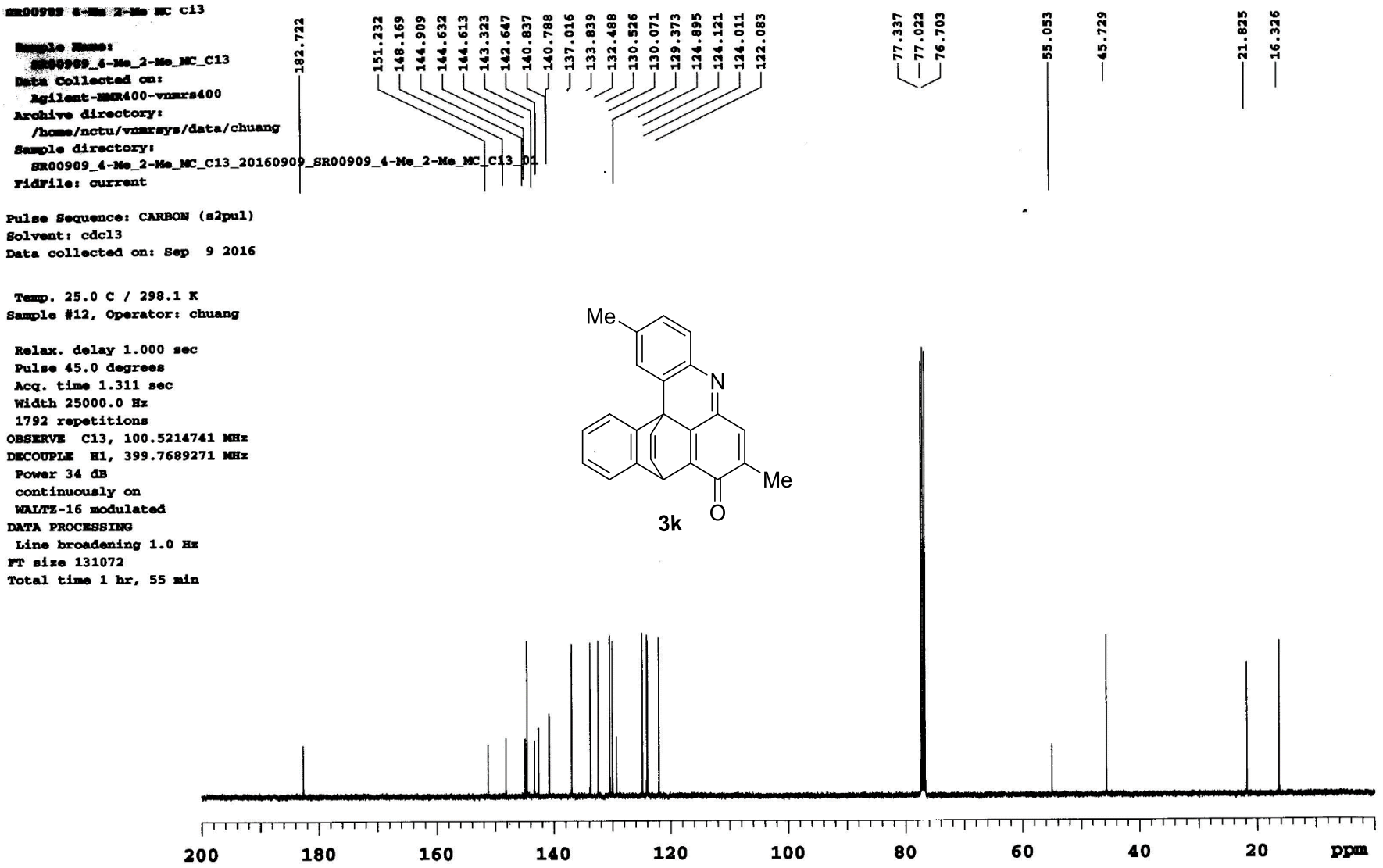


Figure S37. ^{1}H-NMR spectrum of compound **3l** ($CDCl_3$,100 MHz)

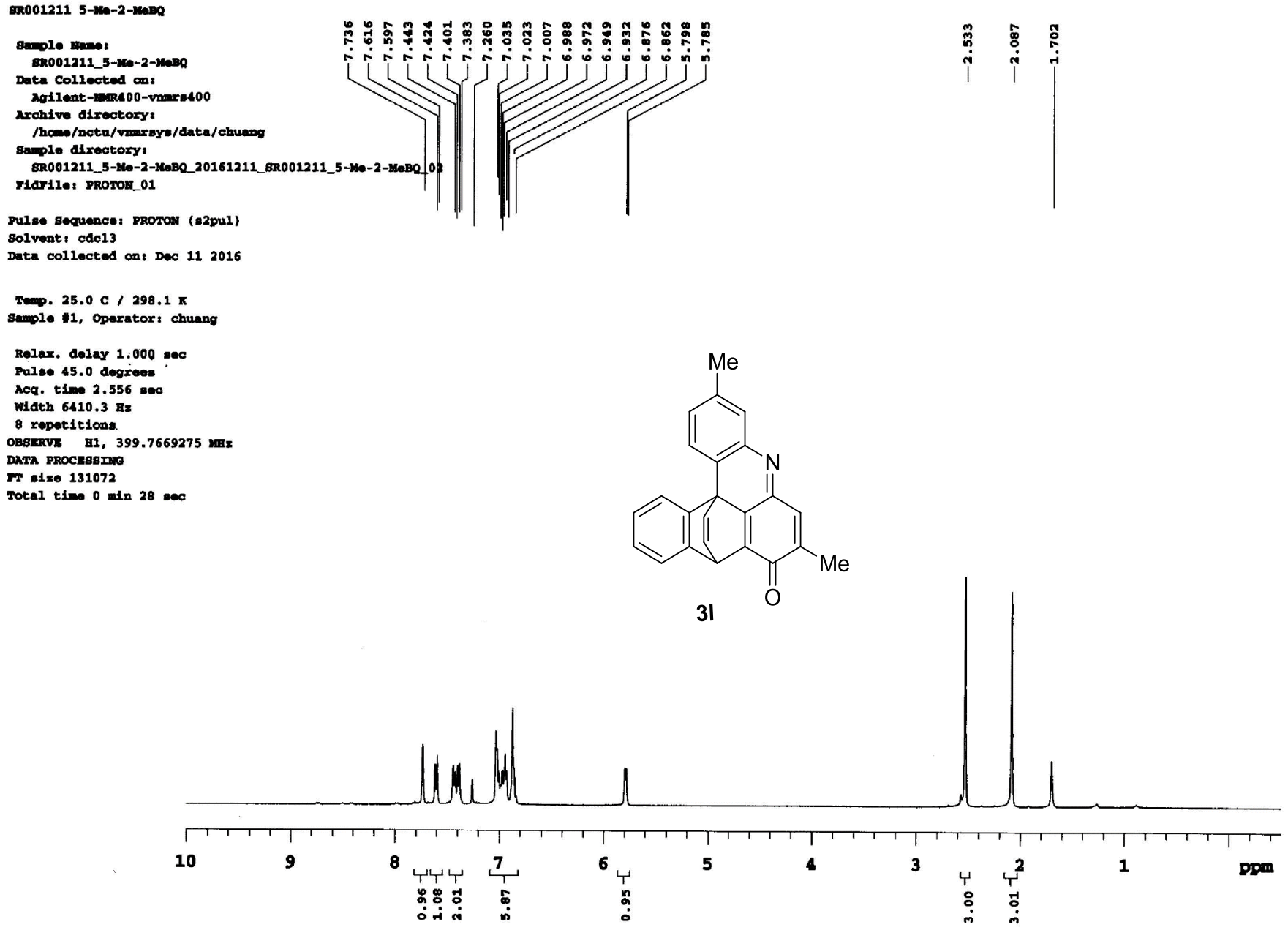


Figure S38. ^{13}C-NMR spectrum of compound **3l** ($CDCl_3$,100 MHz)

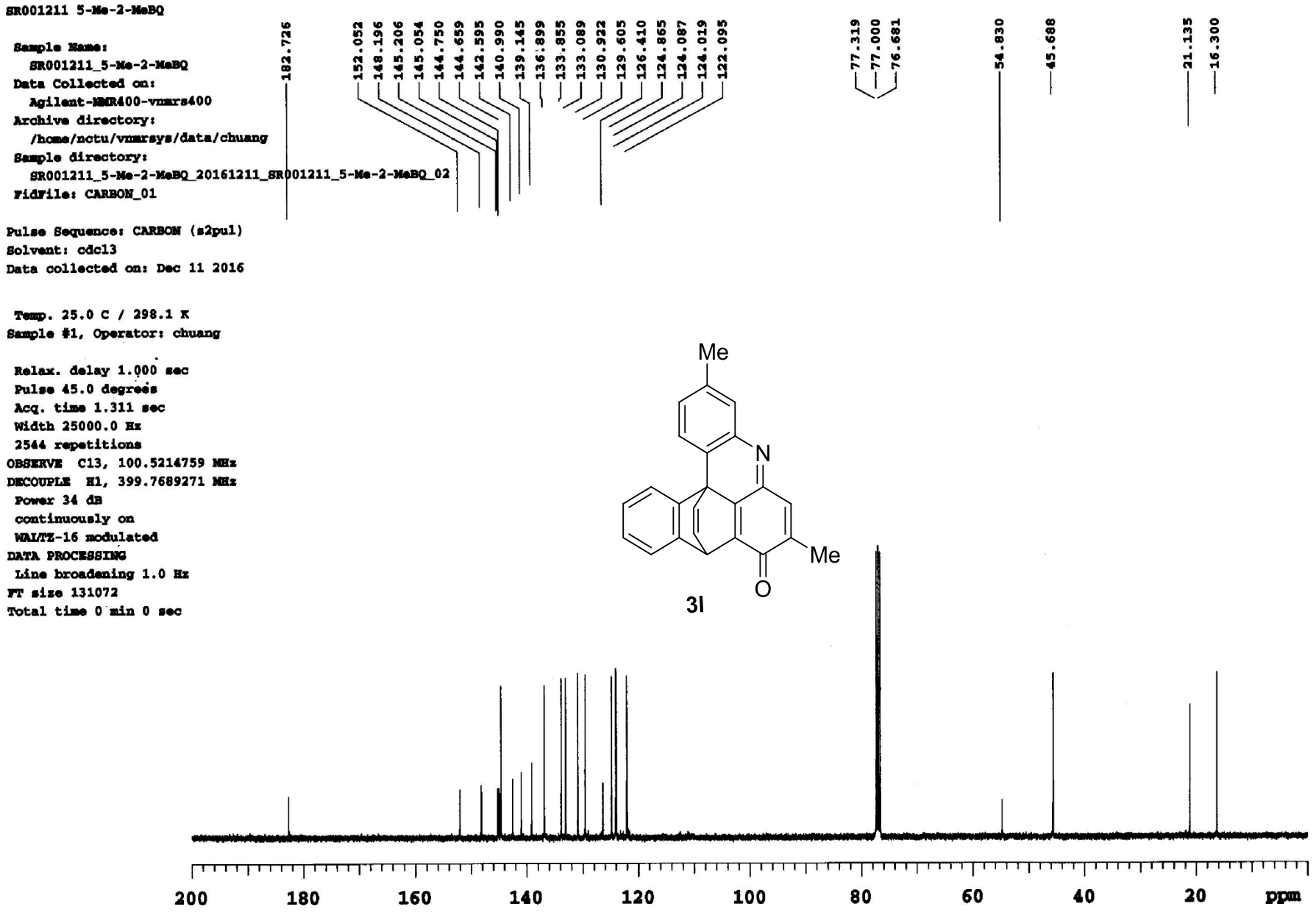


Figure S39. ^{1}H-NMR spectrum of compound **3m** ($CDCl_3$,400 MHz)

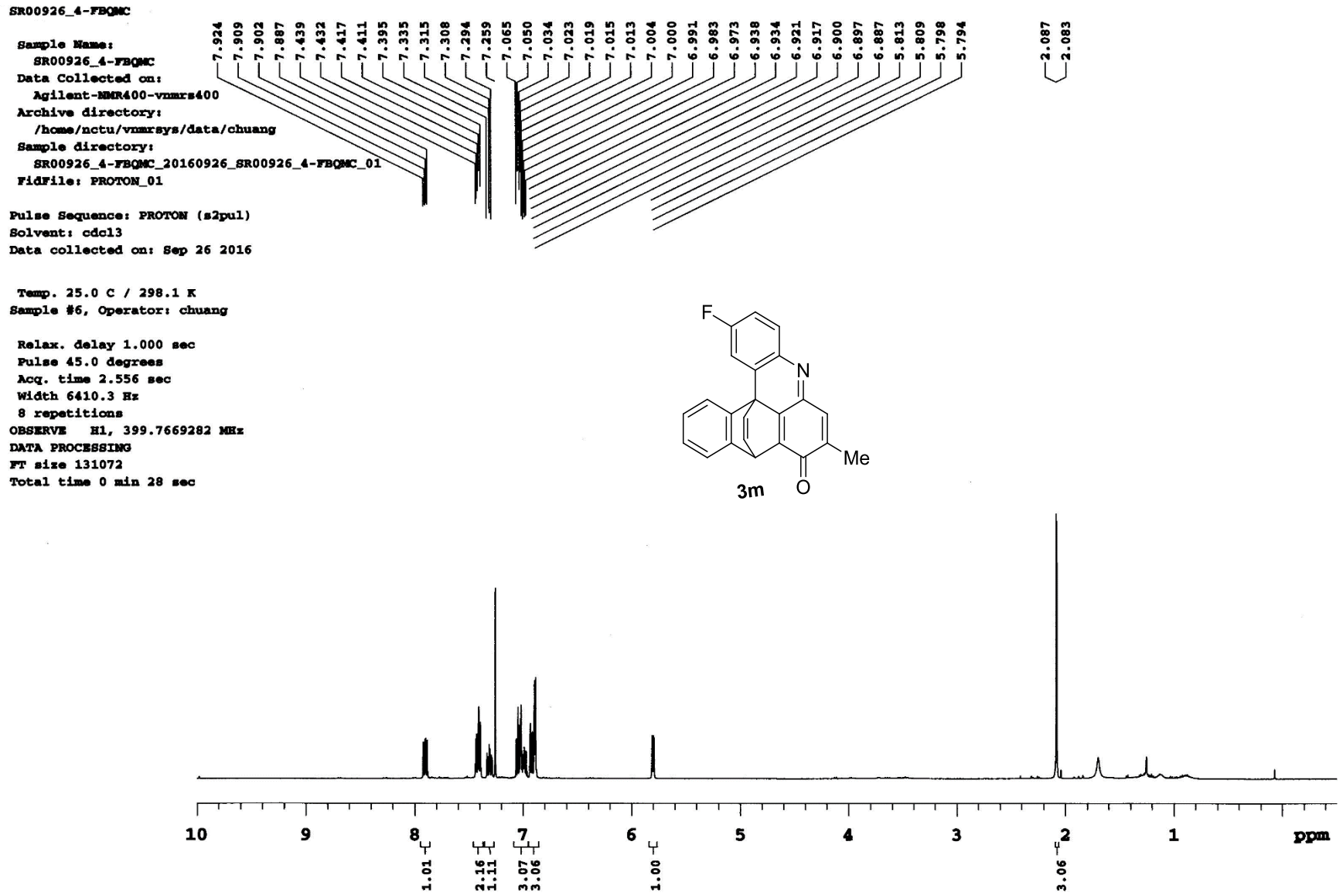


Figure S40. ^{13}C-NMR spectrum of compound **3m** ($CDCl_3$,100 MHz)

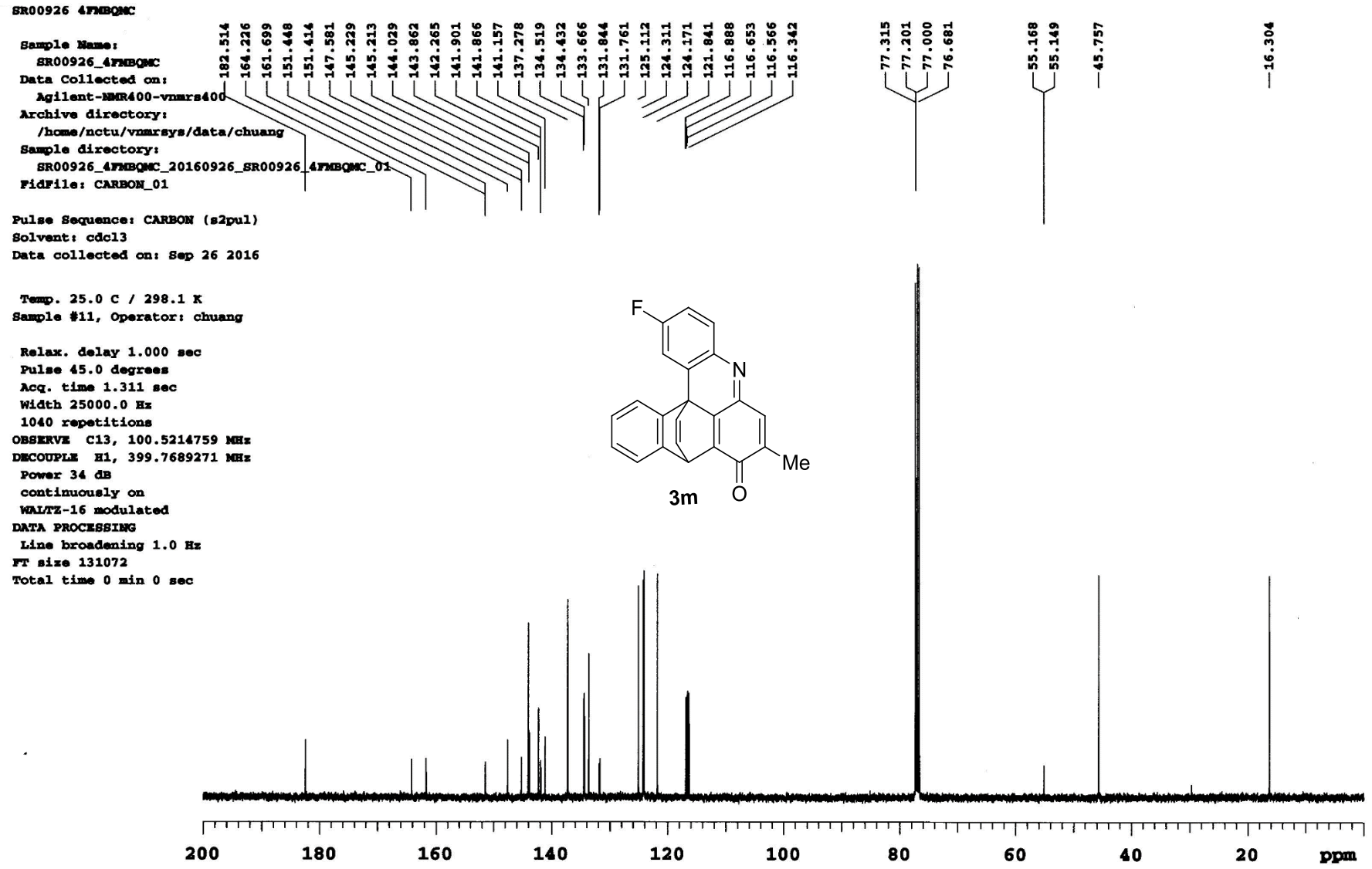


Figure S41. ^{1}H-NMR spectrum of compound **3n** ($CDCl_3$,400 MHz)

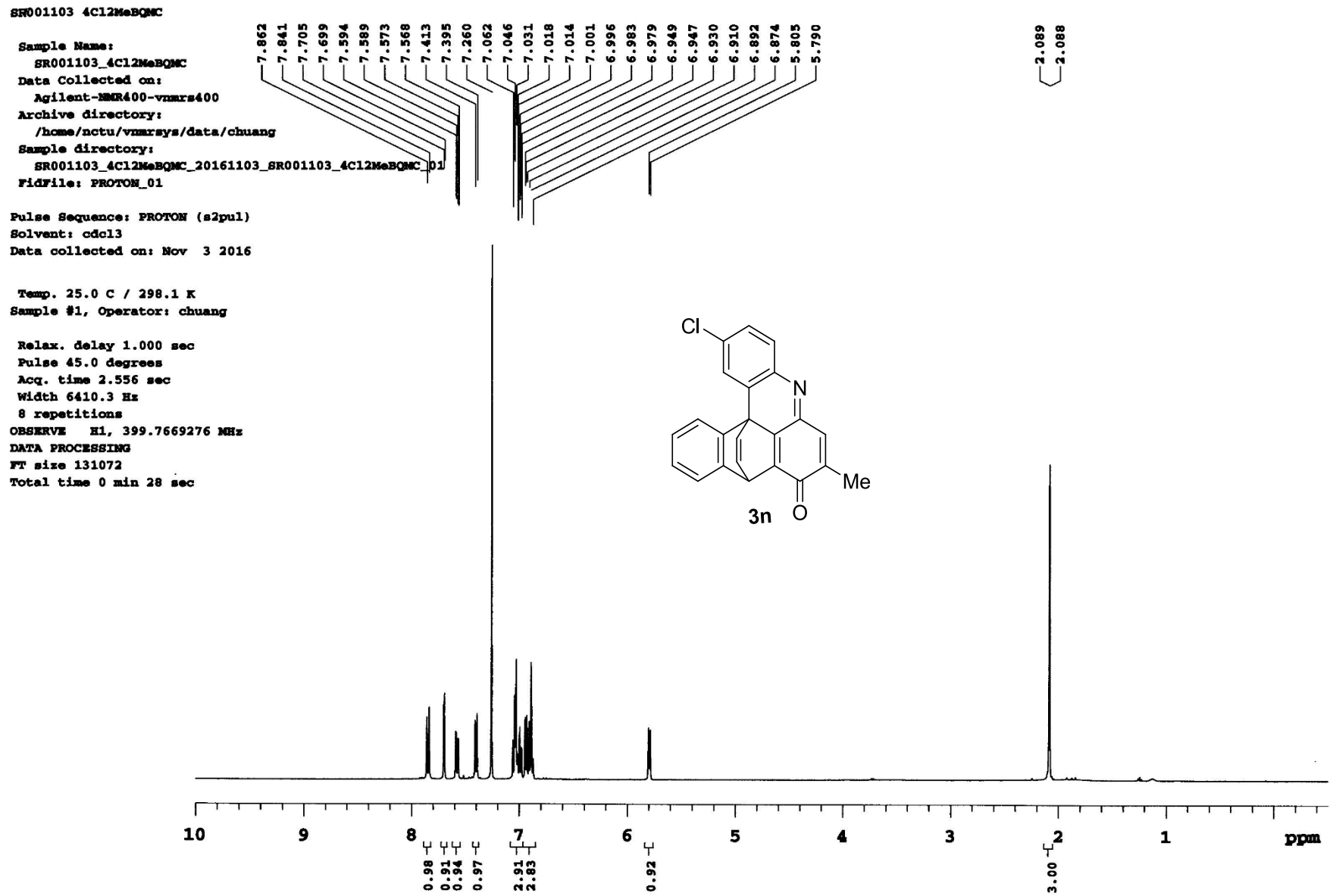


Figure S42. ^{13}C-NMR spectrum of compound **3n** ($CDCl_3$,100 MHz)

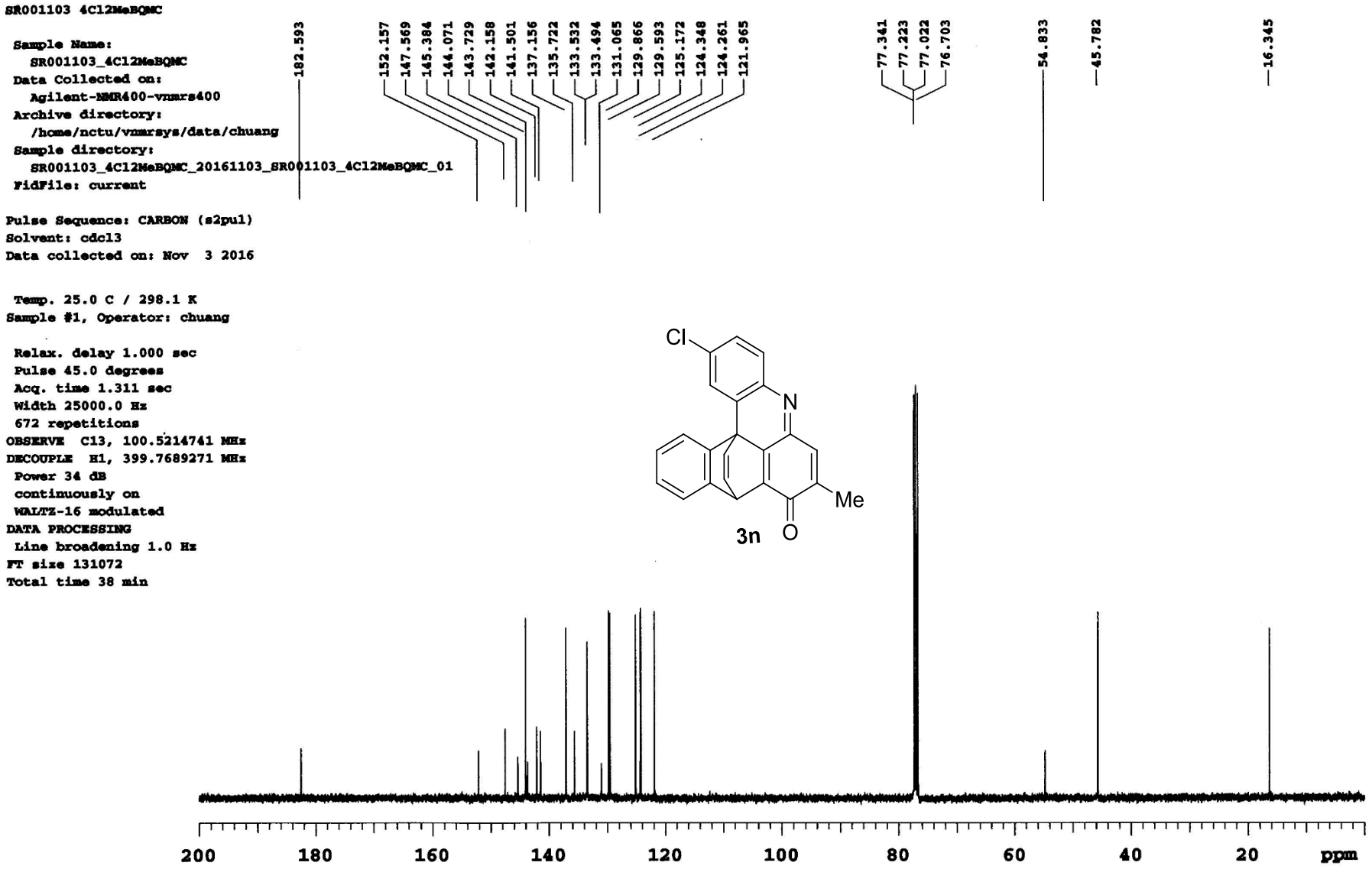


Figure S43. ^{13}C-NMR spectrum of compound **3o** ($CDCl_3$,400 MHz)

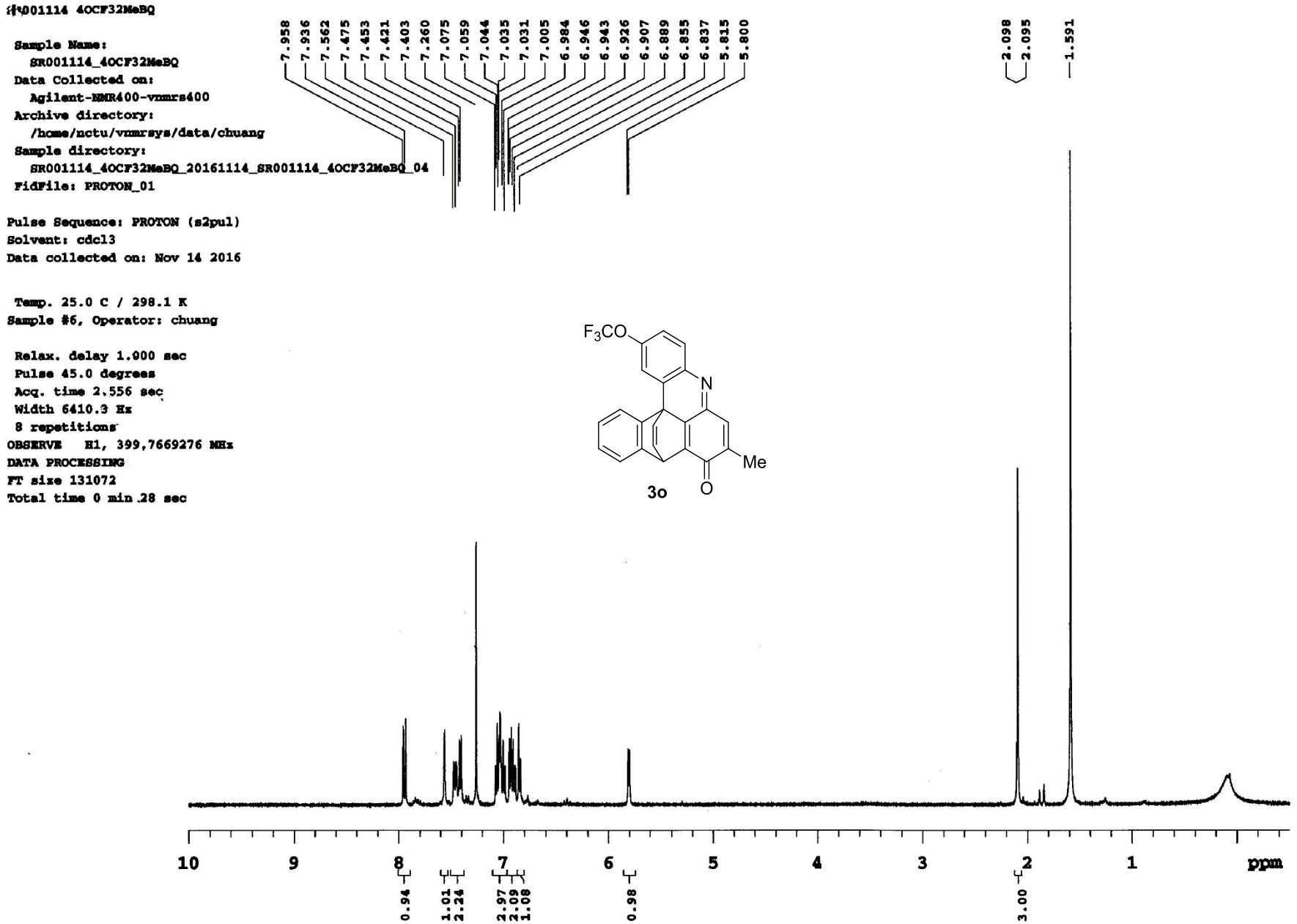


Figure S44. ^{13}C-NMR spectrum of compound **3o** ($CDCl_3$,100 MHz)

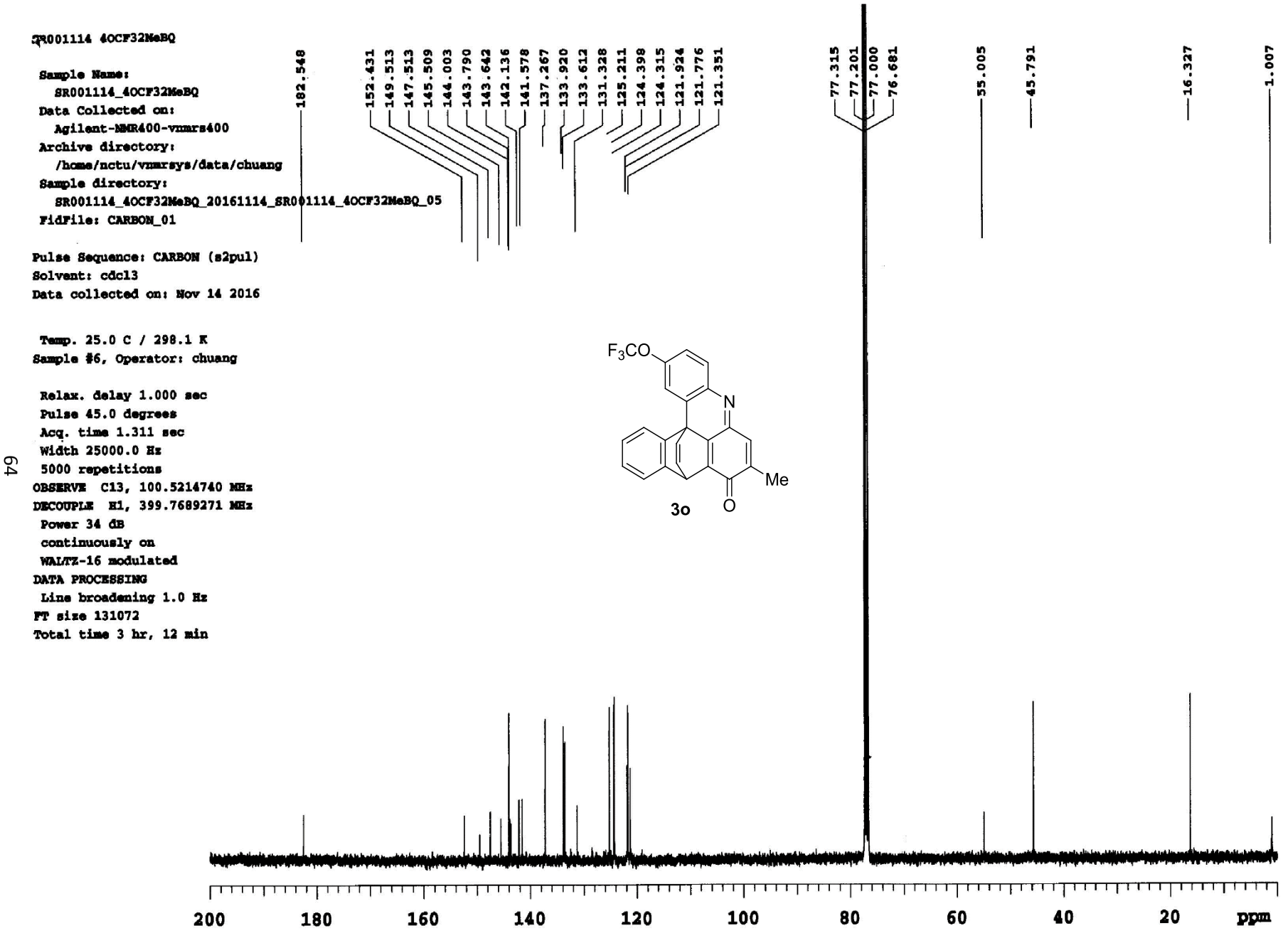


Figure S45. ^{1}H-NMR spectrum of compound **3p** ($CDCl_3$,400 MHz)

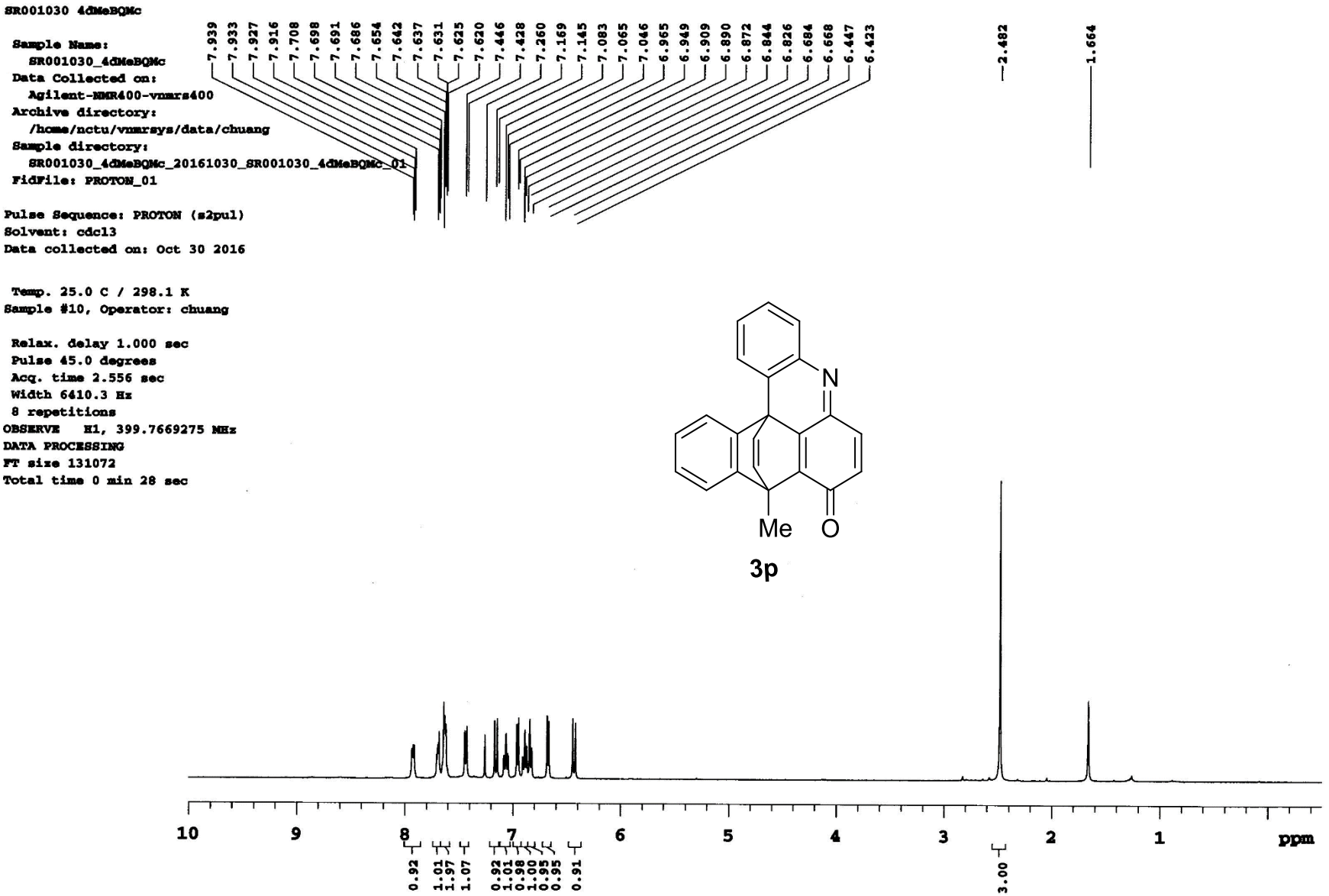


Figure S46. ^{13}C-NMR spectrum of compound **3p** ($CDCl_3$,100 MHz)

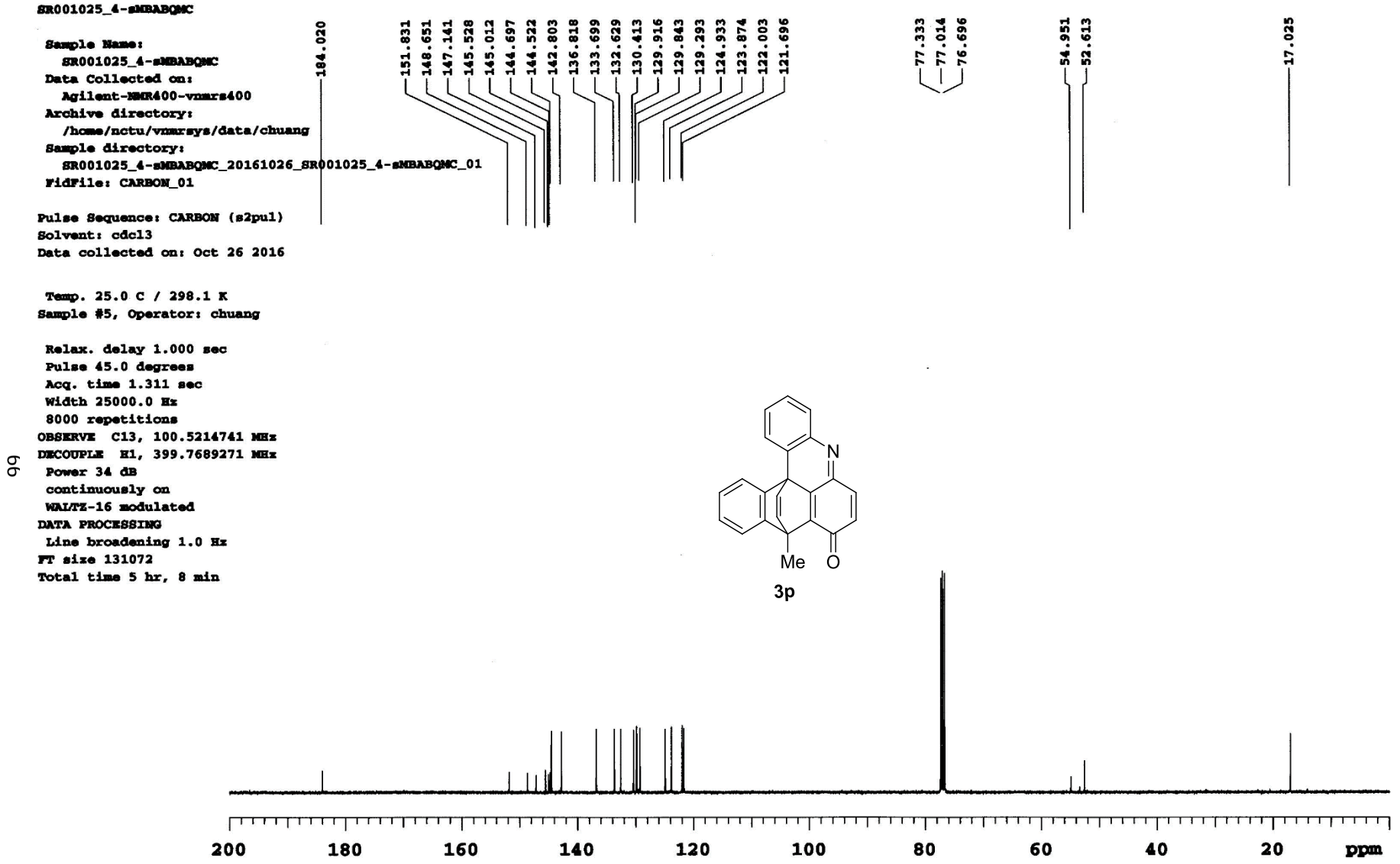


Figure S47. ^{1}H-NMR spectrum of compound **3q** ($CDCl_3$,400 MHz)

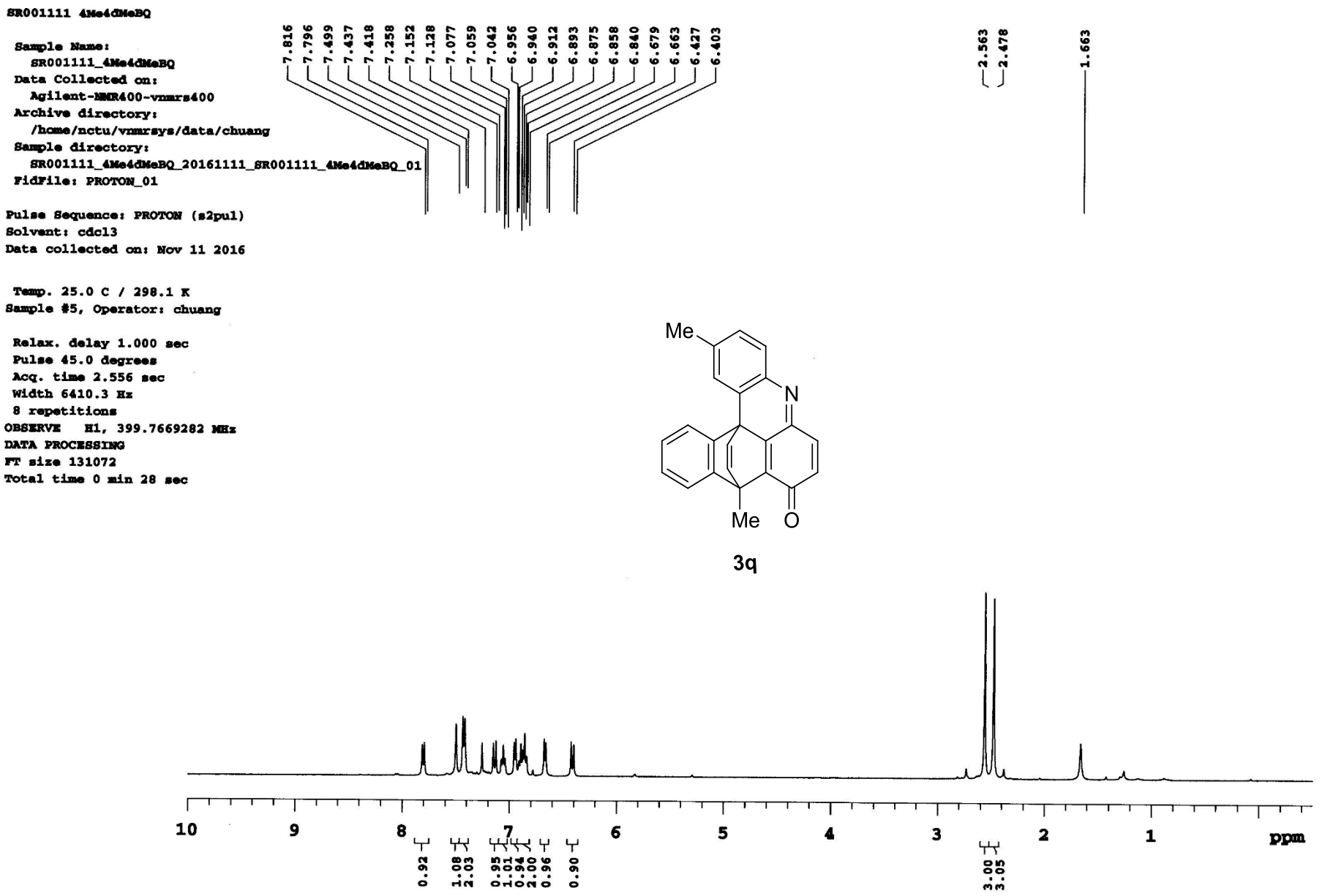


Figure S48. ^{13}C-NMR spectrum of compound **3q** ($CDCl_3$,100 MHz)

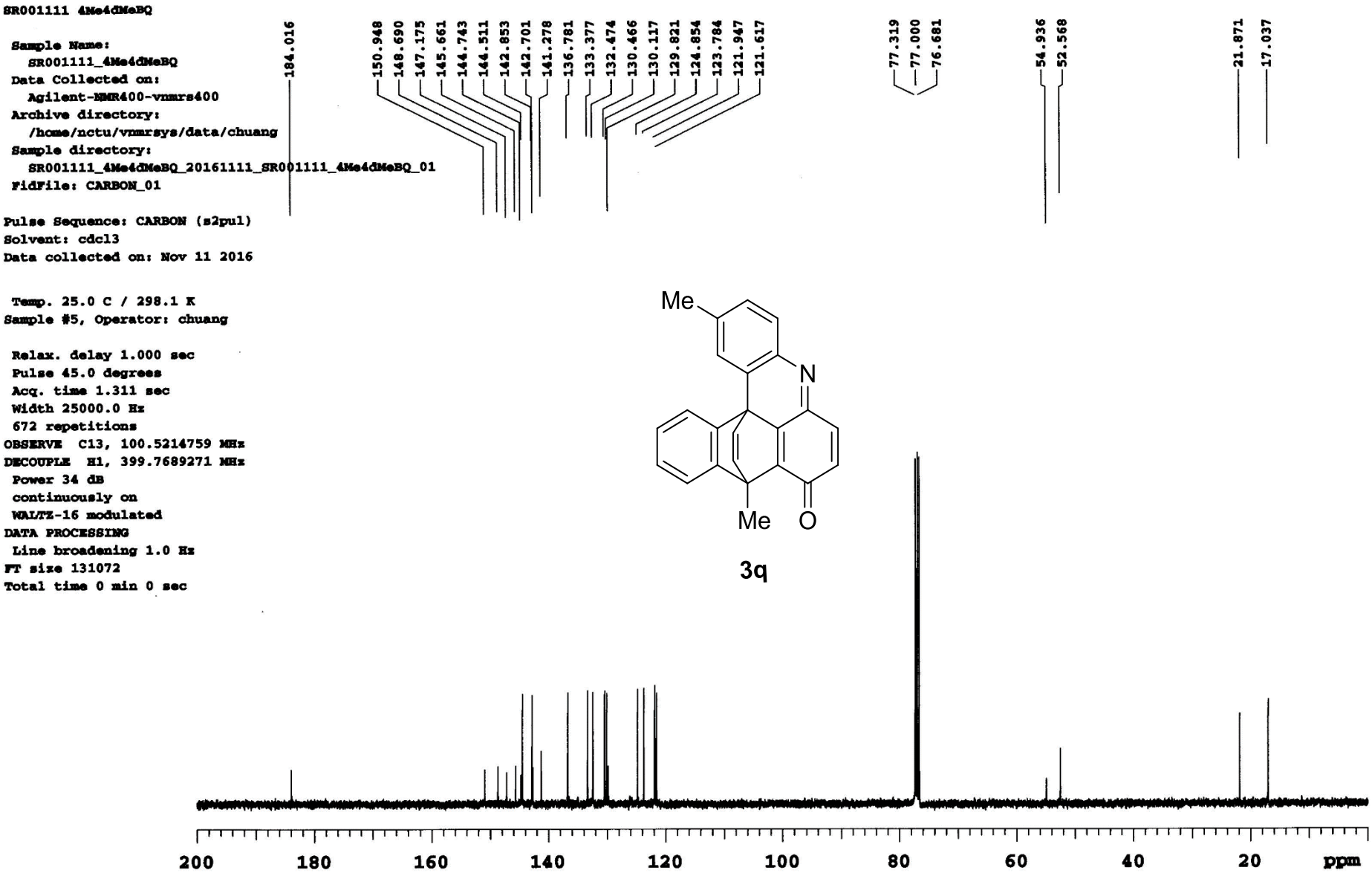


Figure S49. ^{1}H-NMR spectrum of compound **3r** ($CDCl_3$,400 MHz)

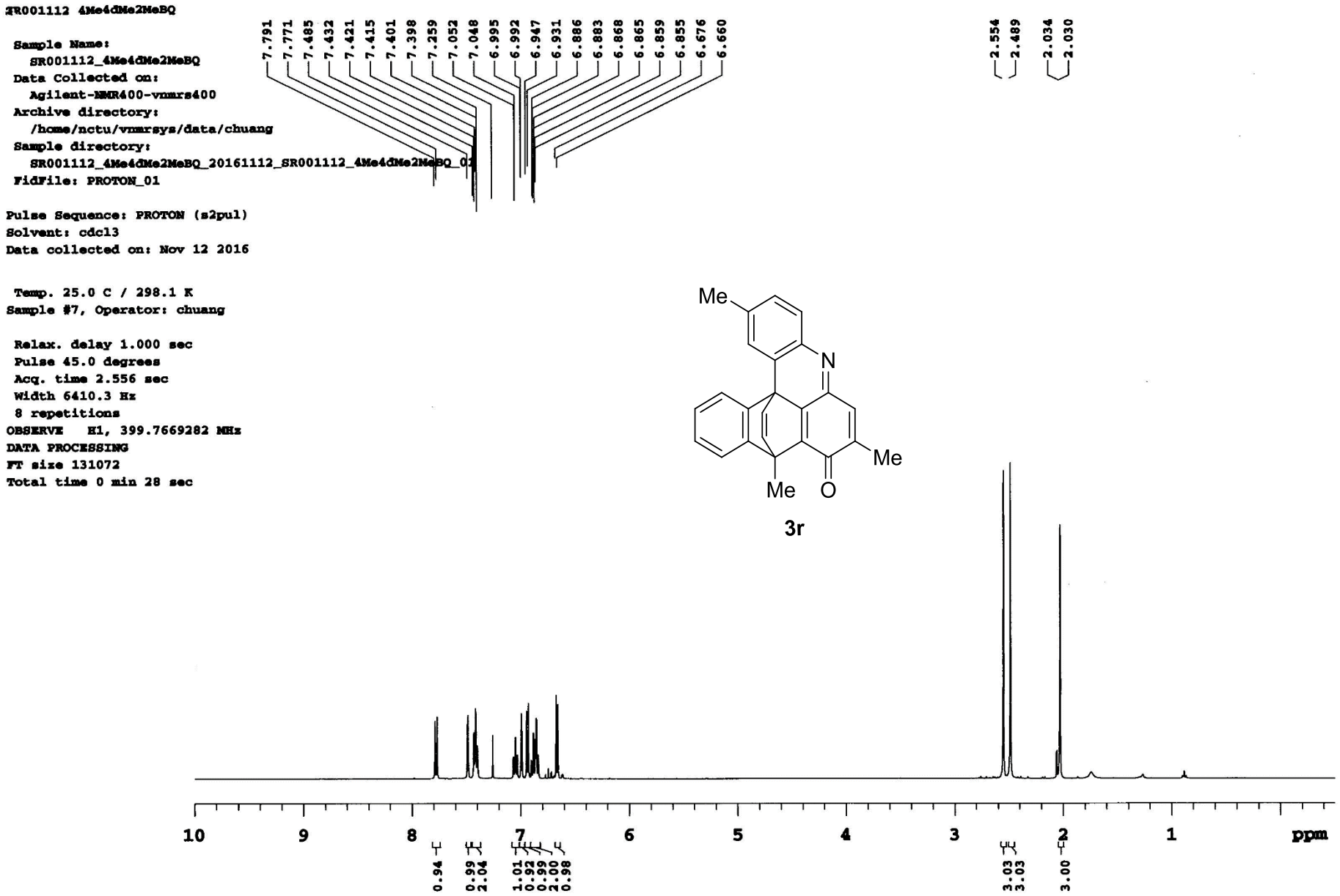


Figure S50. ^{13}C-NMR spectrum of compound **3r** ($CDCl_3$,100 MHz)

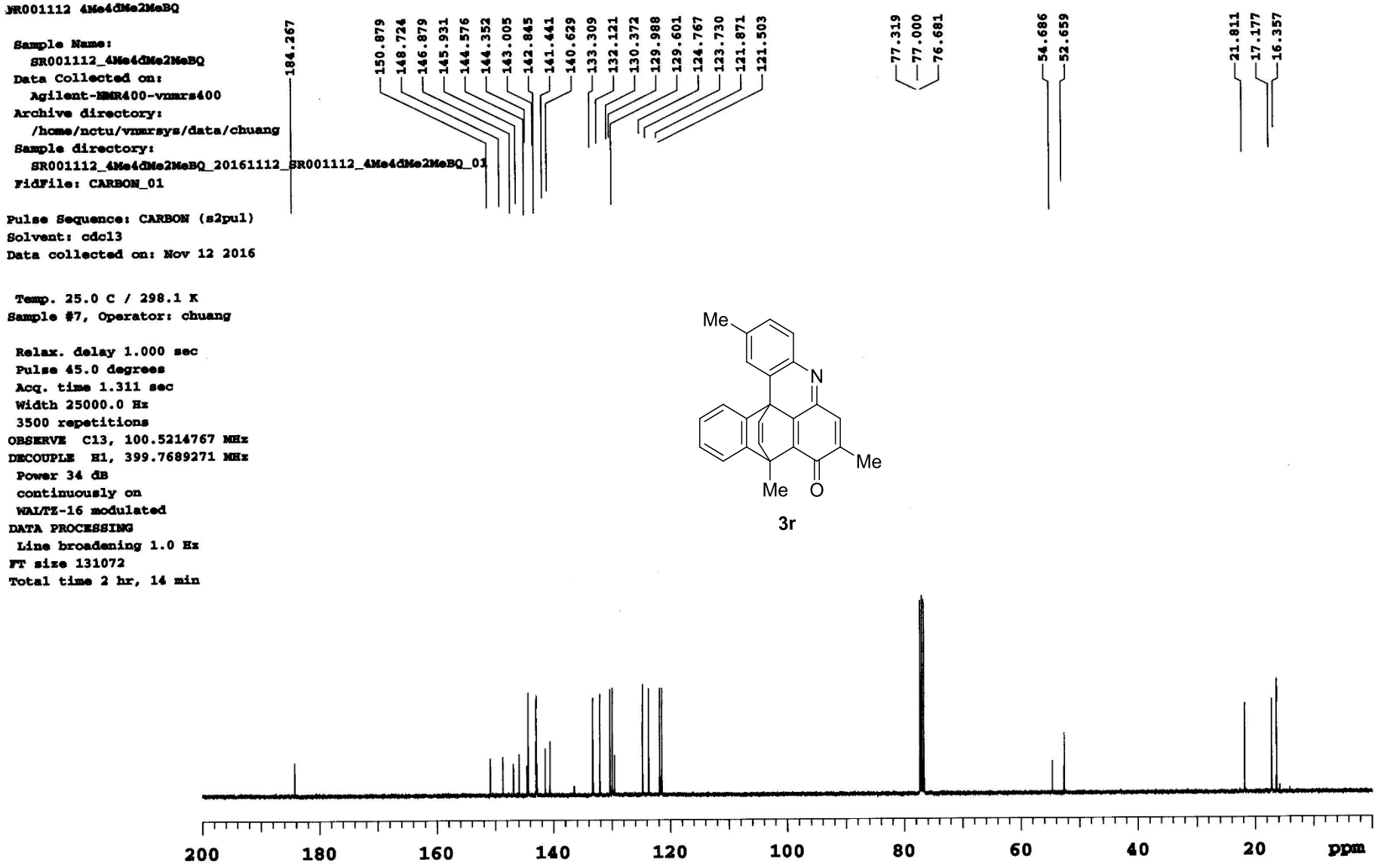


Figure S51. ^{1}H-NMR spectrum of compound **3s** ($CDCl_3$,400 MHz)

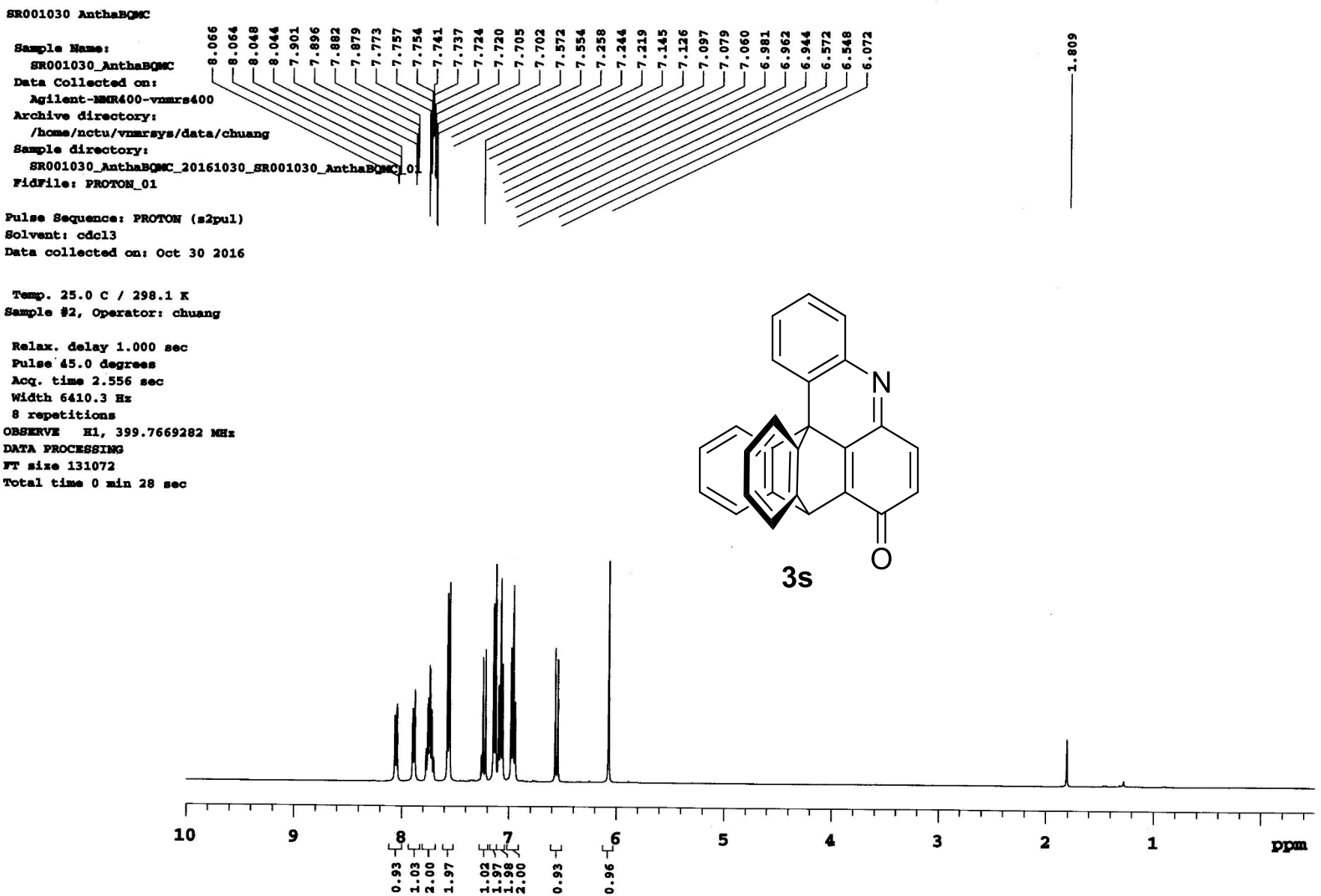


Figure S52. ^{13}C-NMR spectrum of compound **3s** ($CDCl_3$,100 MHz)

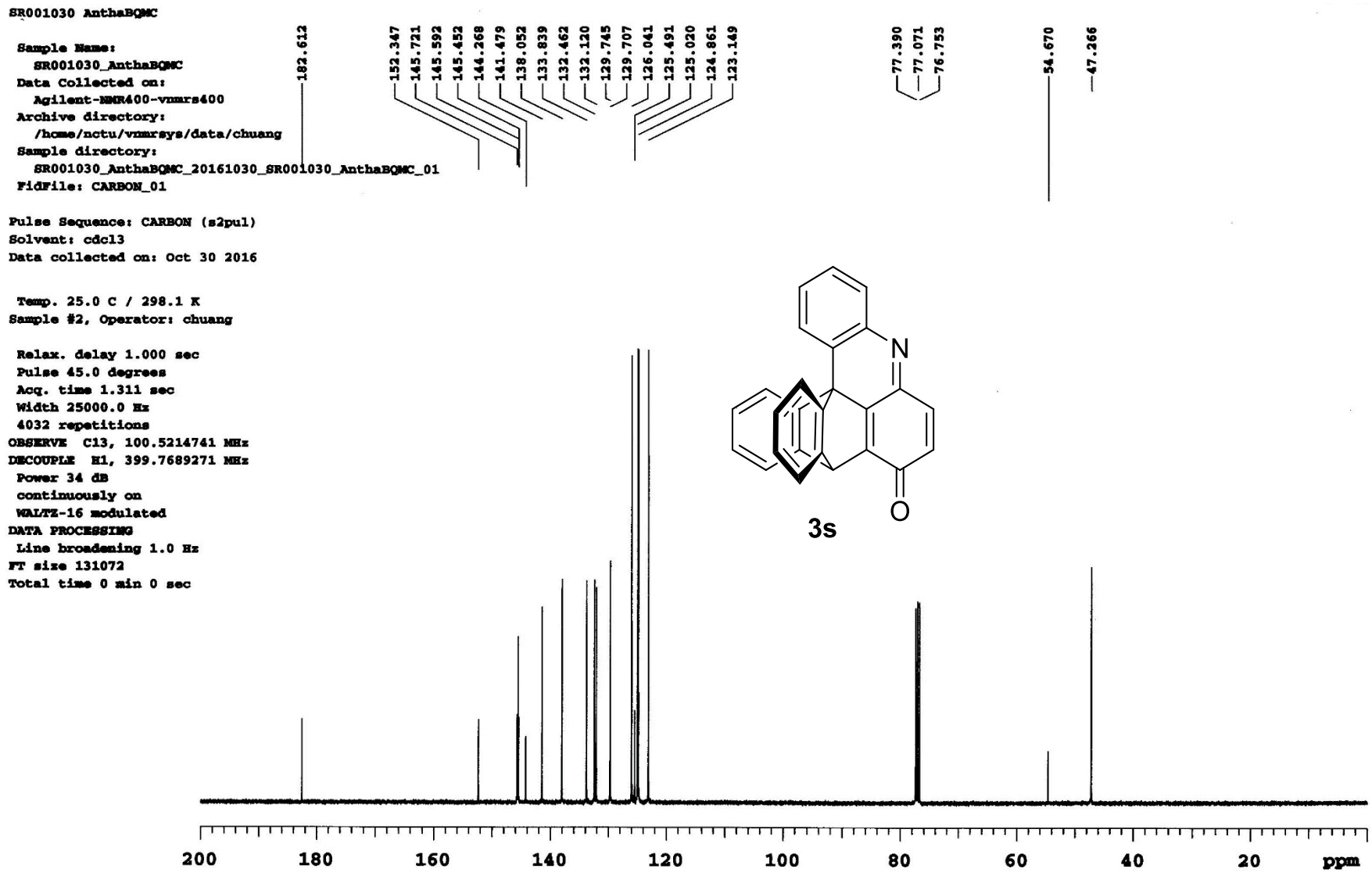


Figure S53. ^{1}H-NMR spectrum of compound **3t** ($CDCl_3$,400 MHz)

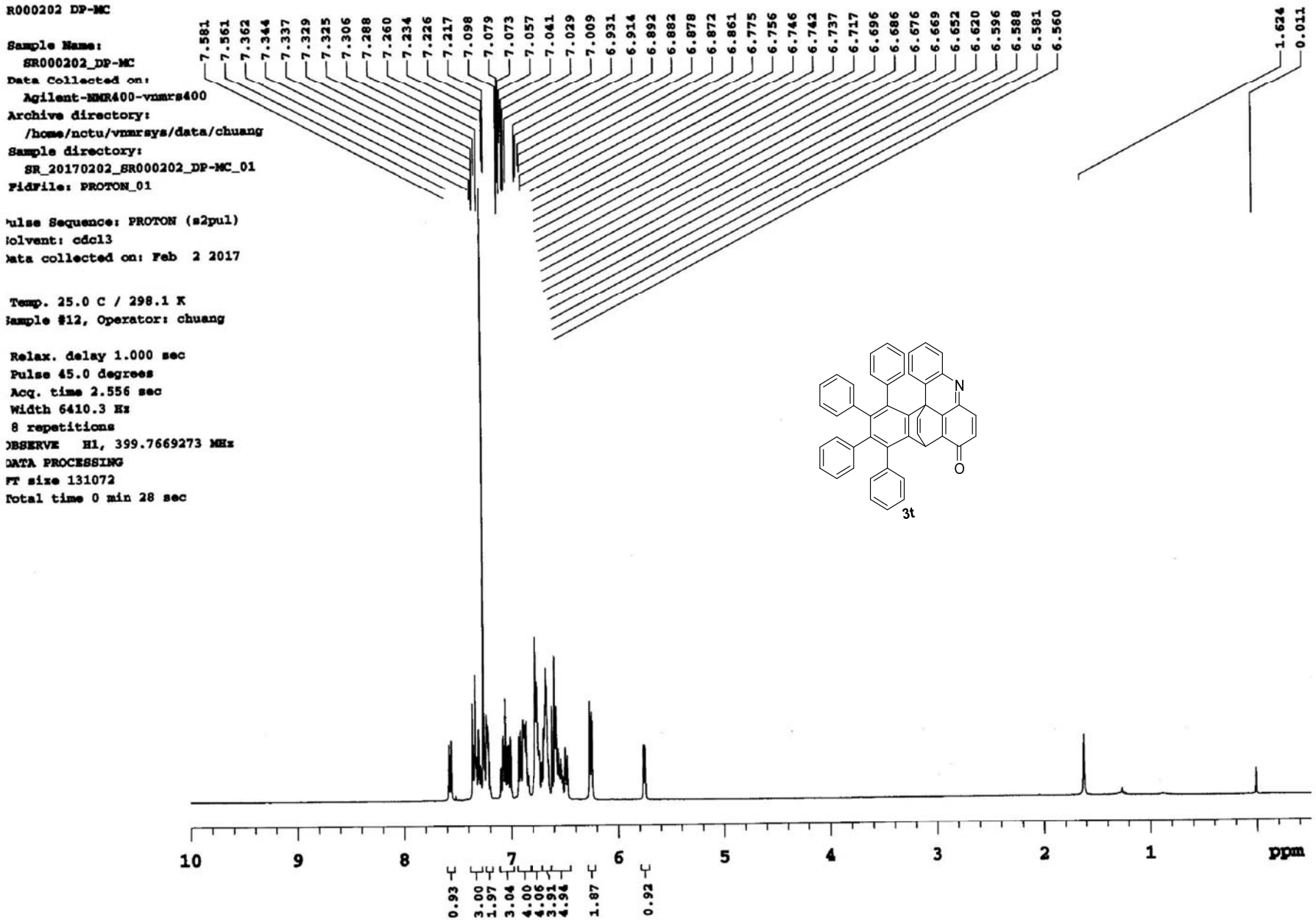


Figure S54. ^{1}H-NMR spectrum of compound **3t** ($CDCl_3$,100 MHz)

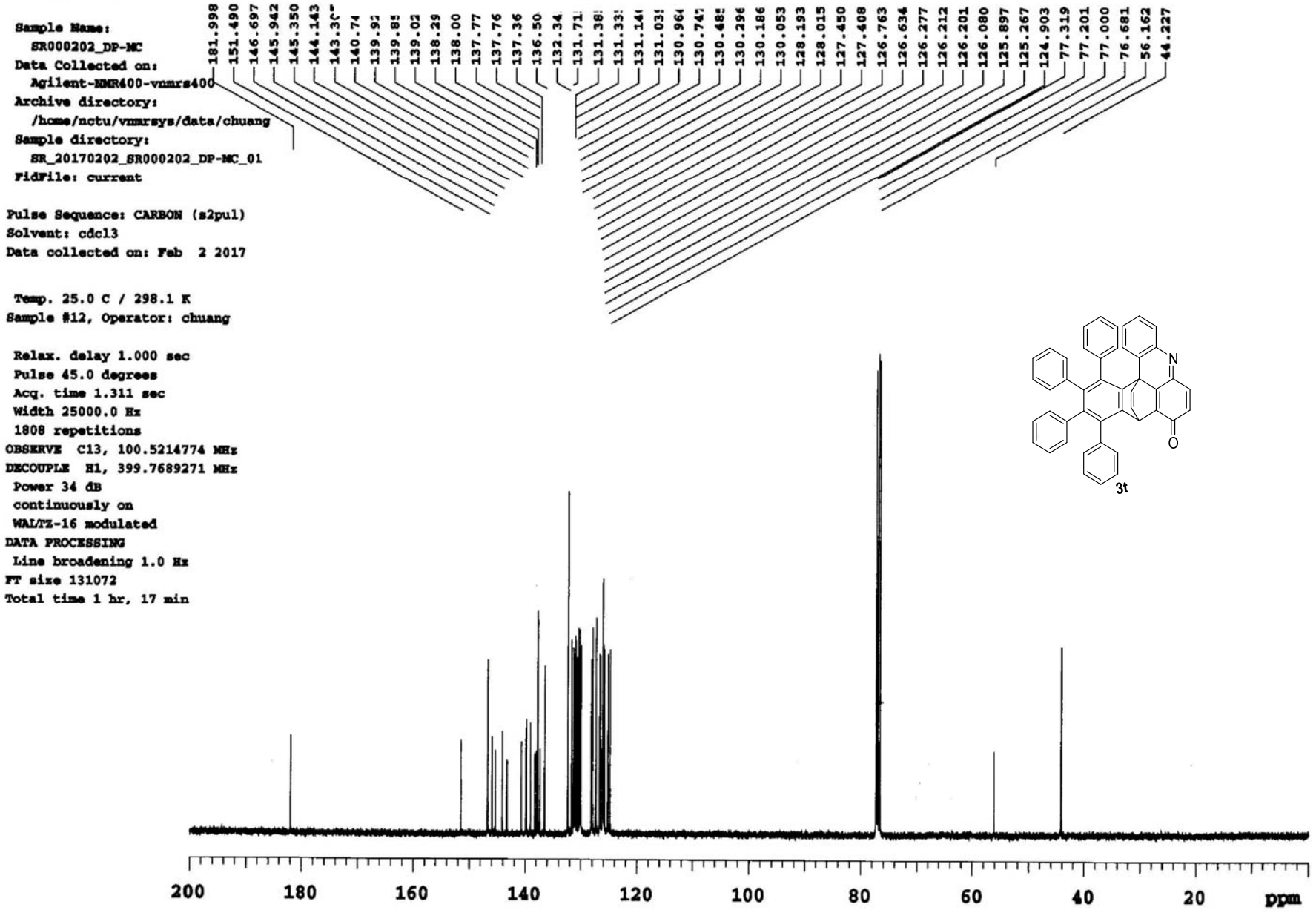


Figure S55. ^{1}H-NMR spectrum of compound **4a** ($CDCl_3$, 400 MHz)

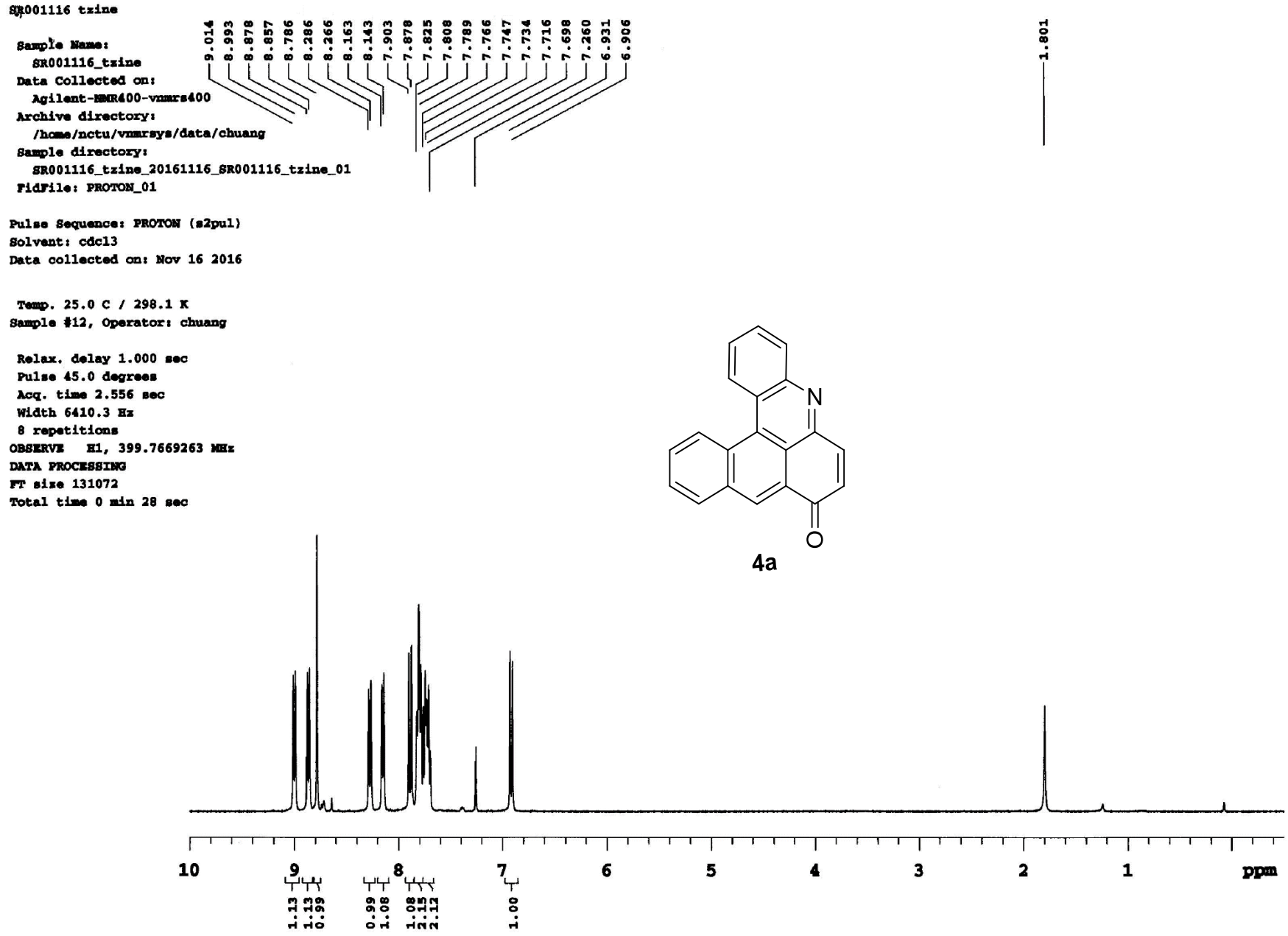


Figure S56. ^{1}H-NMR spectrum of compound **4a**($CDCl_3$, 100 MHz)

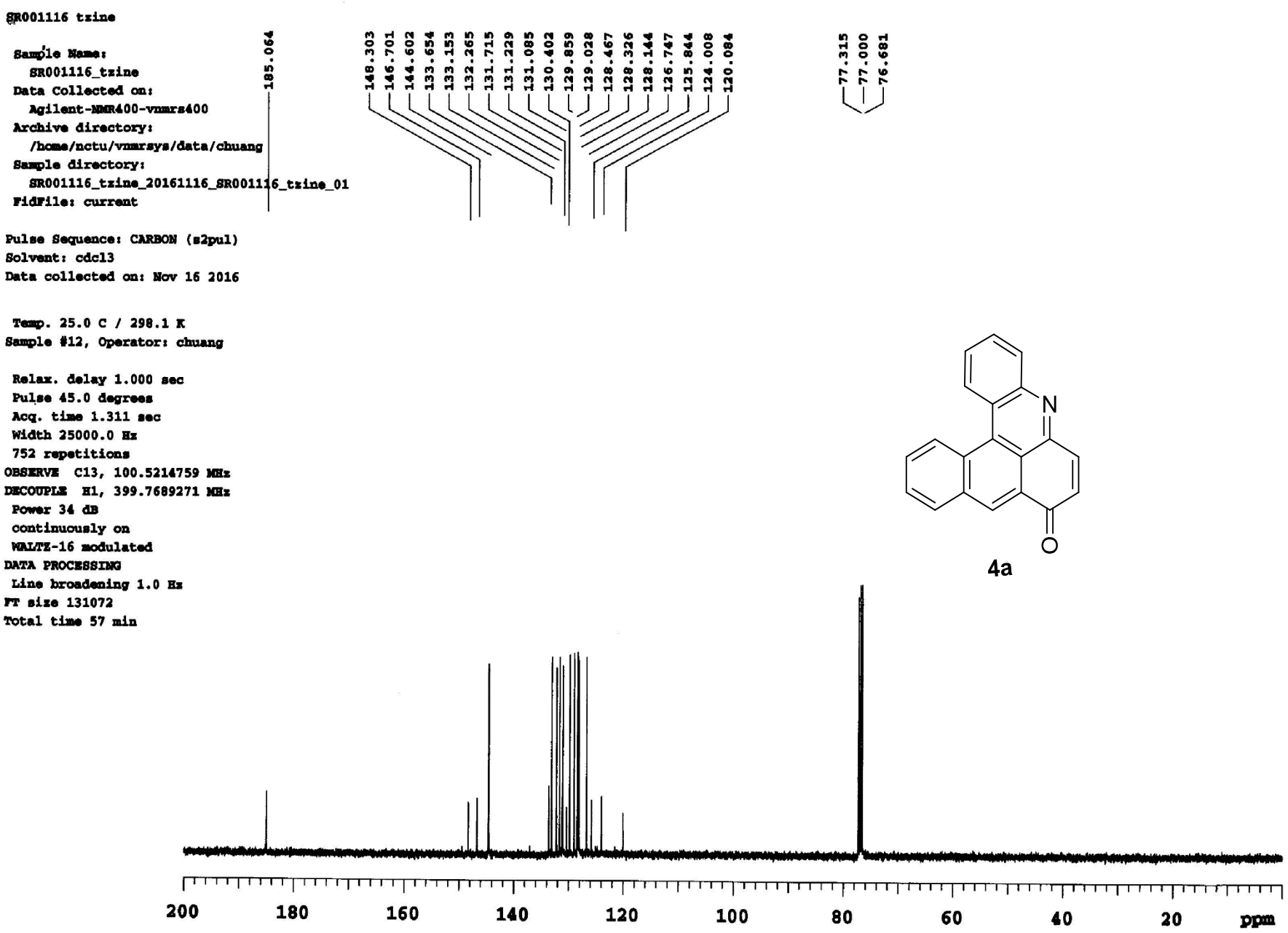


Figure S57. ^{1}H-NMR spectrum of compound **4b**($CDCl_3$, 700 MHz)

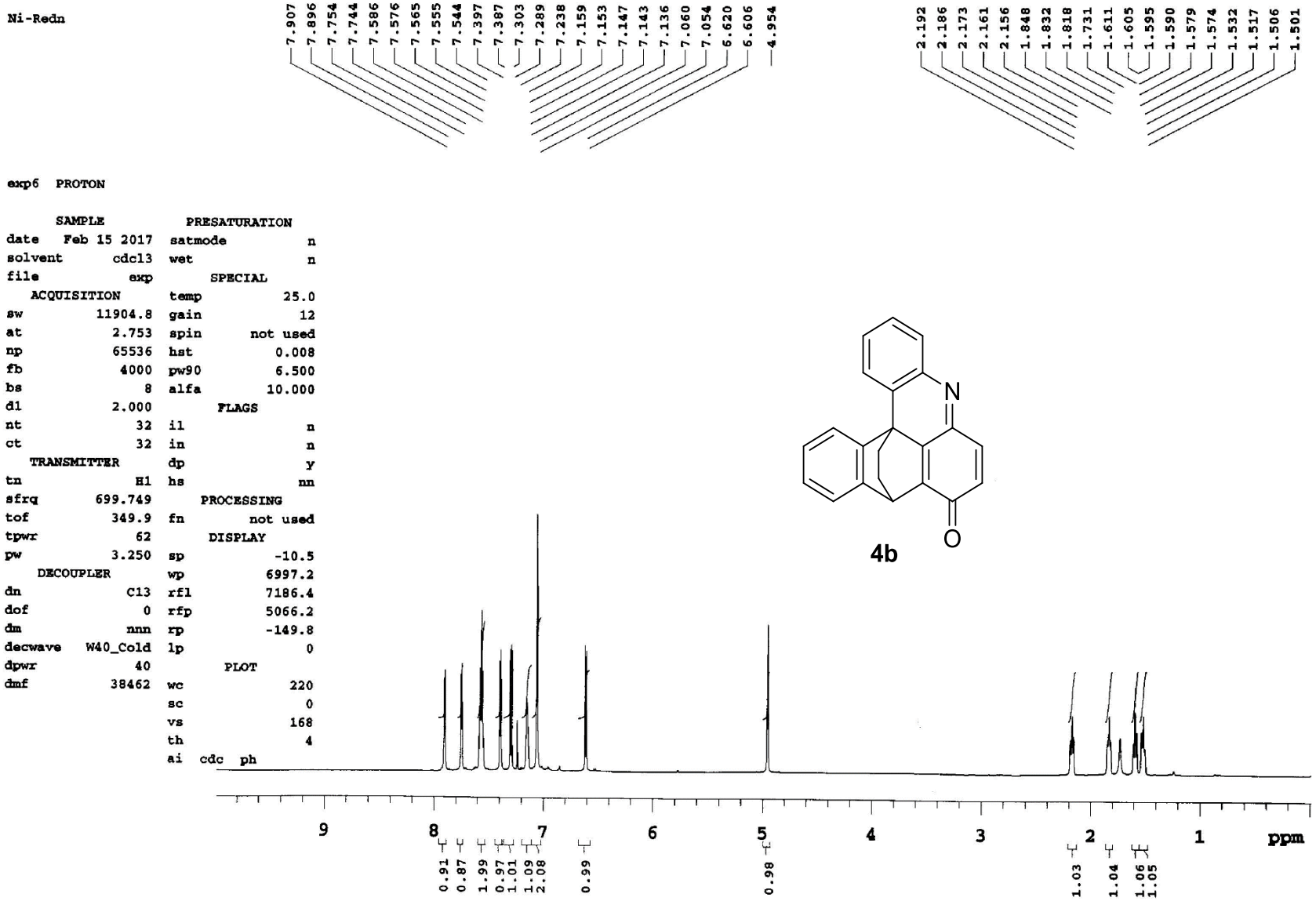


Figure S58. ^{13}C-NMR spectrum of compound **4b**($CDCl_3$, 175 MHz)

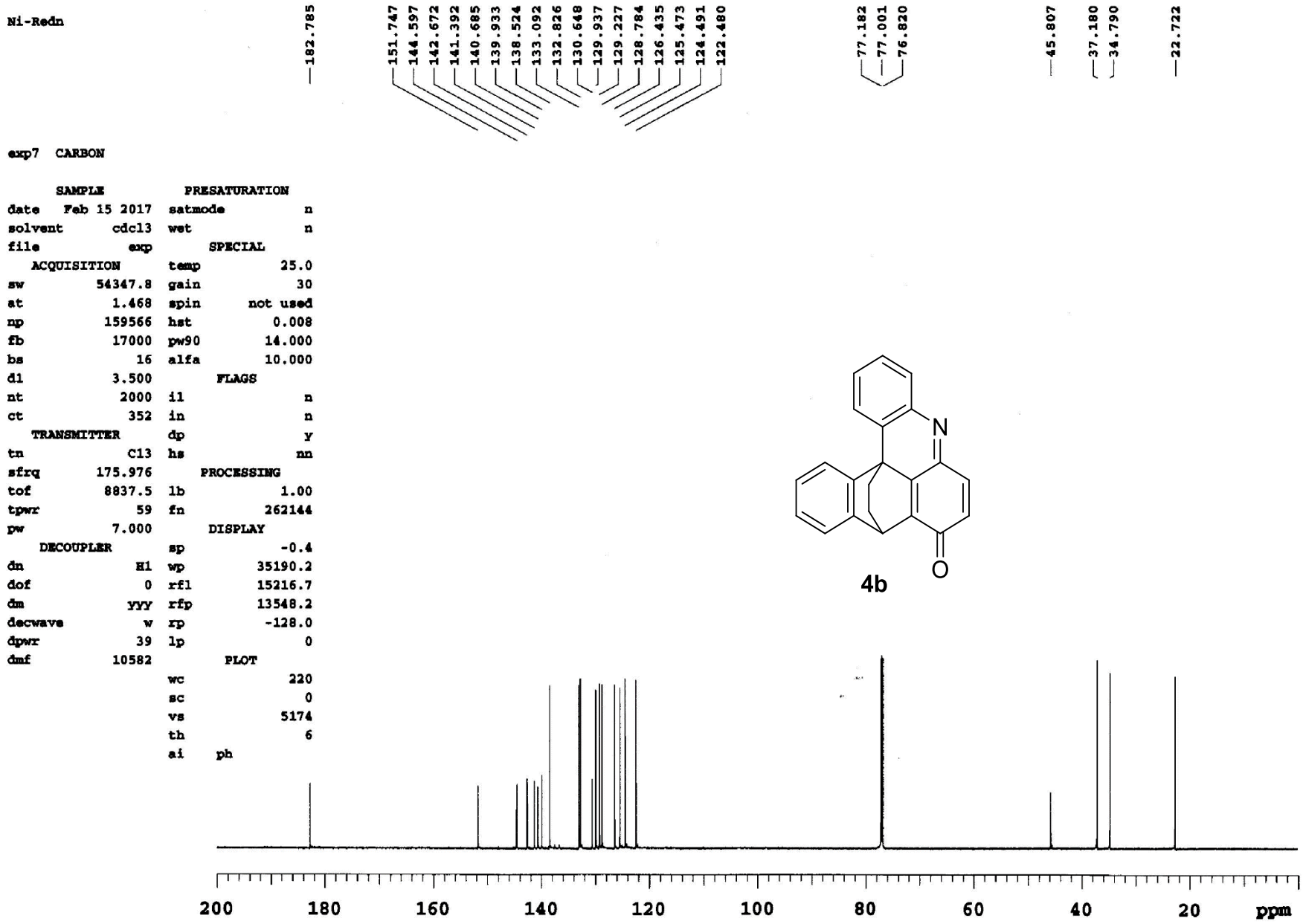


Figure S59. ^{1}H-NMR spectrum of compound **4c** ($CDCl_3$, 400 MHz)

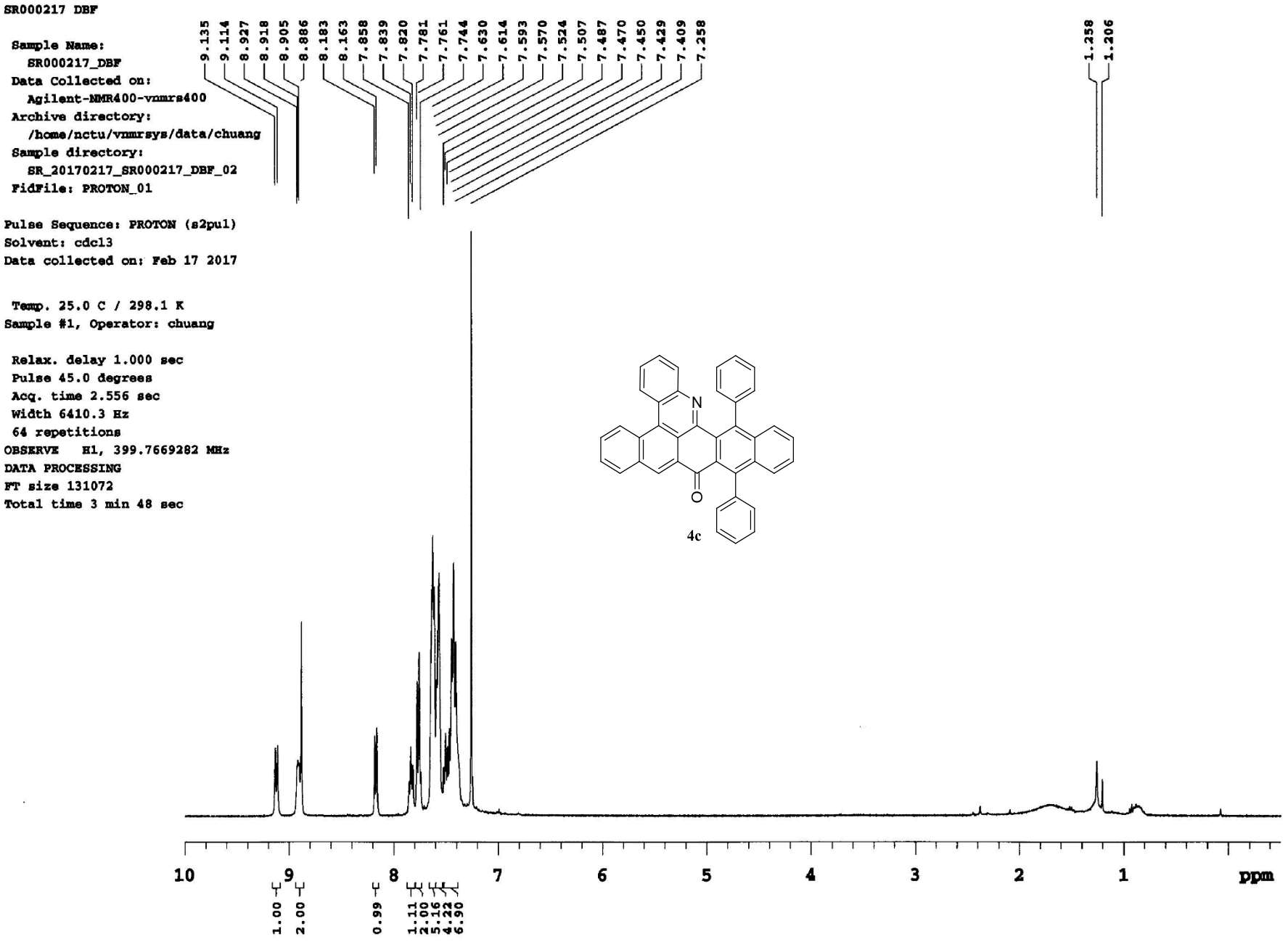


Figure S60. ^{13}C-NMR spectrum of compound **4c** ($CDCl_3$, 100 MHz)

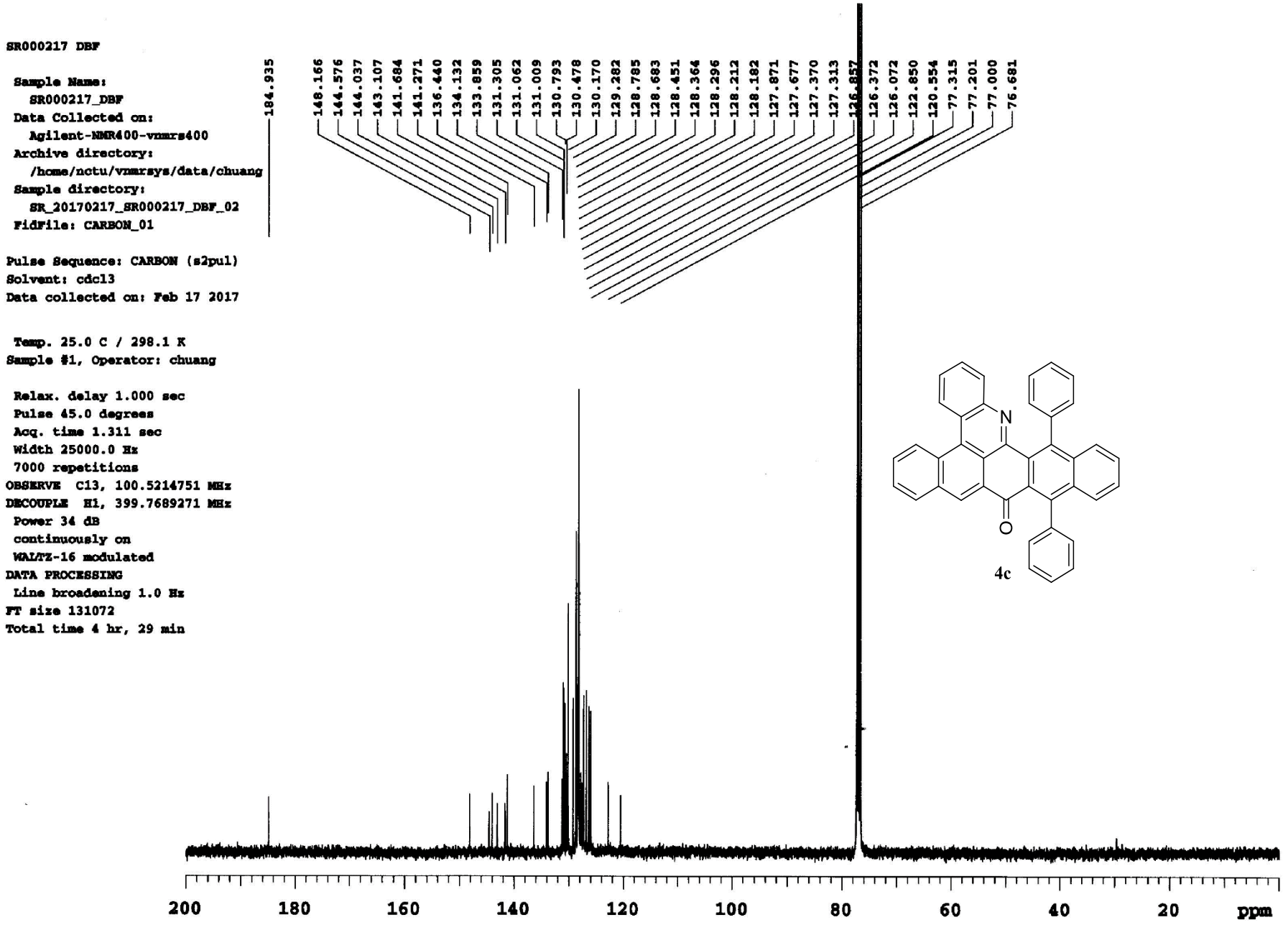


Figure S61. ^{1}H-NMR spectrum of compound **4d** (CD_2Cl_2, 400 MHz)

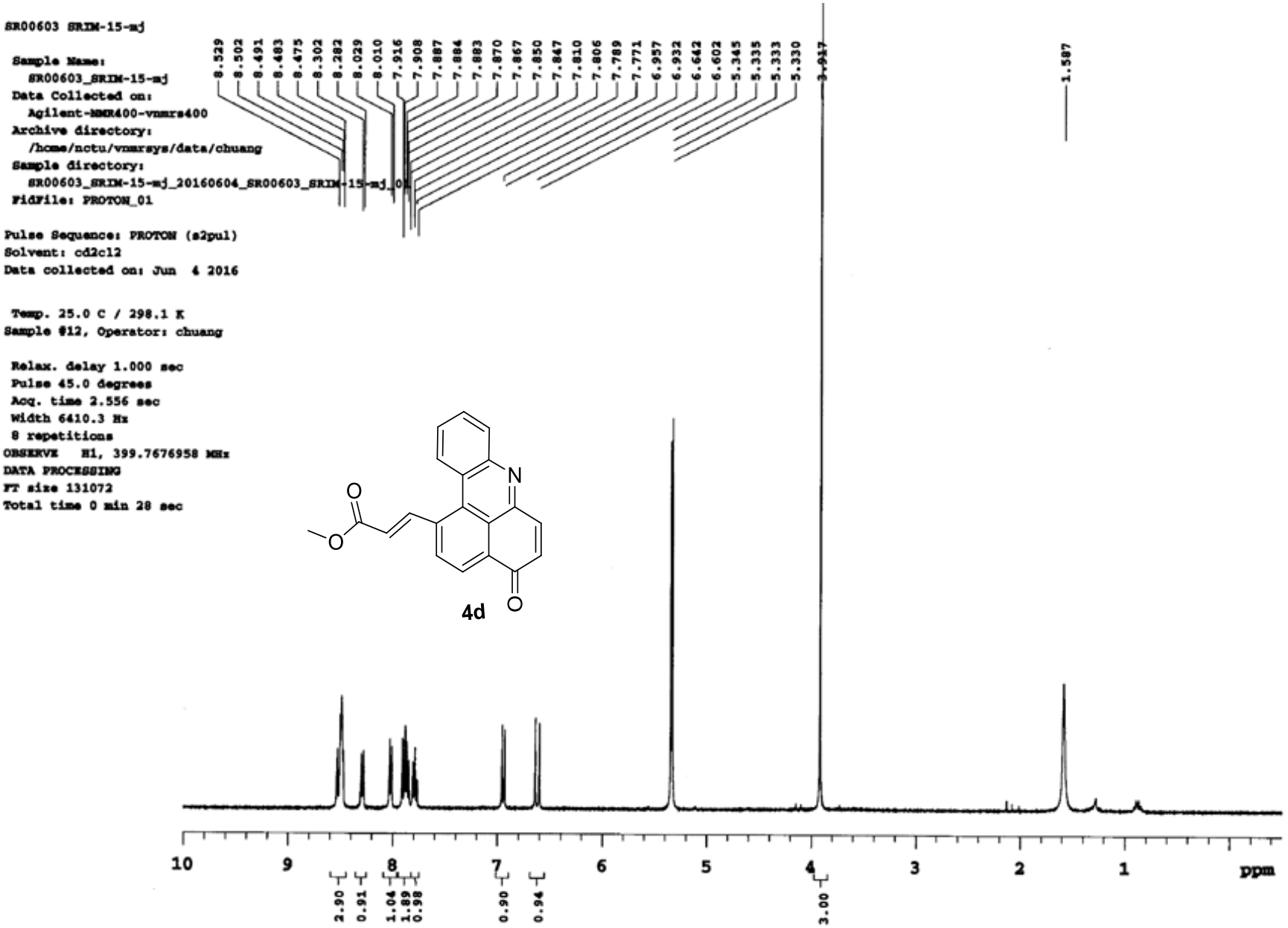


Figure S62. ^{13}C-NMR spectrum of compound **4d** (CD_2Cl_2, 100 MHz)

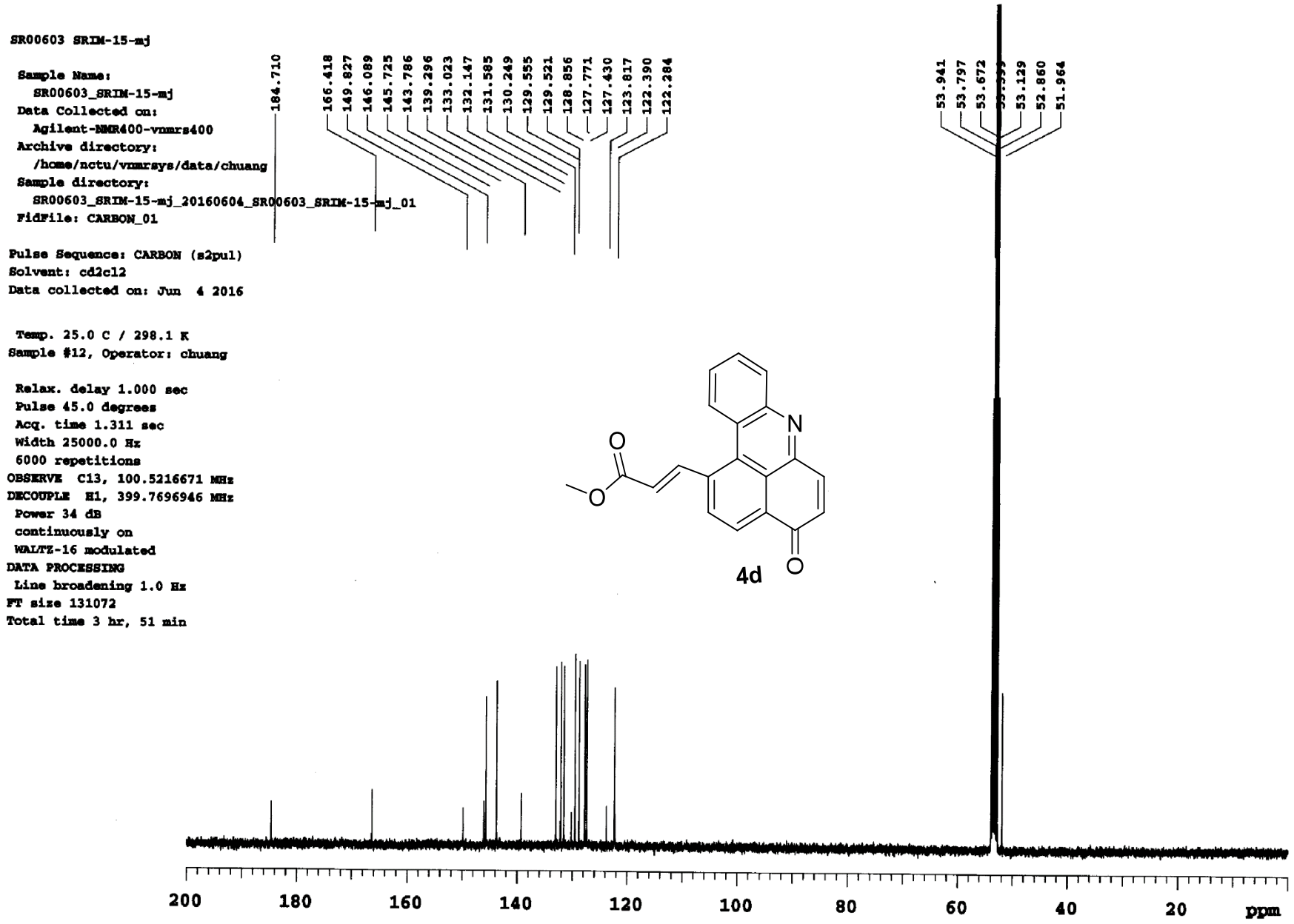


Table S1. Crystal data for compound **3e** (CCDC 1539211).

Empirical formula	C23 H15 N O	
Formula weight	321.36	
Temperature	200(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.1825(6) Å	α= 111.633(7)°.
	b = 9.9928(7) Å	β= 90.794(6)°.
	c = 10.0713(8) Å	γ = 112.965(6)°.
Volume	777.41(10) $Å^3$	
Z	2	
Density (calculated)	1.373 Mg/m^3	
Absorption coefficient	0.657 mm^{-1}	
F(000)	336	
Crystal size	0.25 x 0.20 x 0.15 mm^3	
Theta range for data collection	4.81 to 68.00°.	
Index ranges	-7<=h<=11, -12<=k<=10, -12<=l<=12	
Reflections collected	5077	
Independent reflections	2805 [R(int) = 0.0303]	
Completeness to theta = 68.00°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.92384	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2805 / 0 / 226	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.0541, wR2 = 0.1412	
R indices (all data)	R1 = 0.0719, wR2 = 0.1615	
Largest diff. peak and hole	0.330 and -0.281 e.$Å^{-3}$	

Figure S63. Solid state structure of compound **3e.**

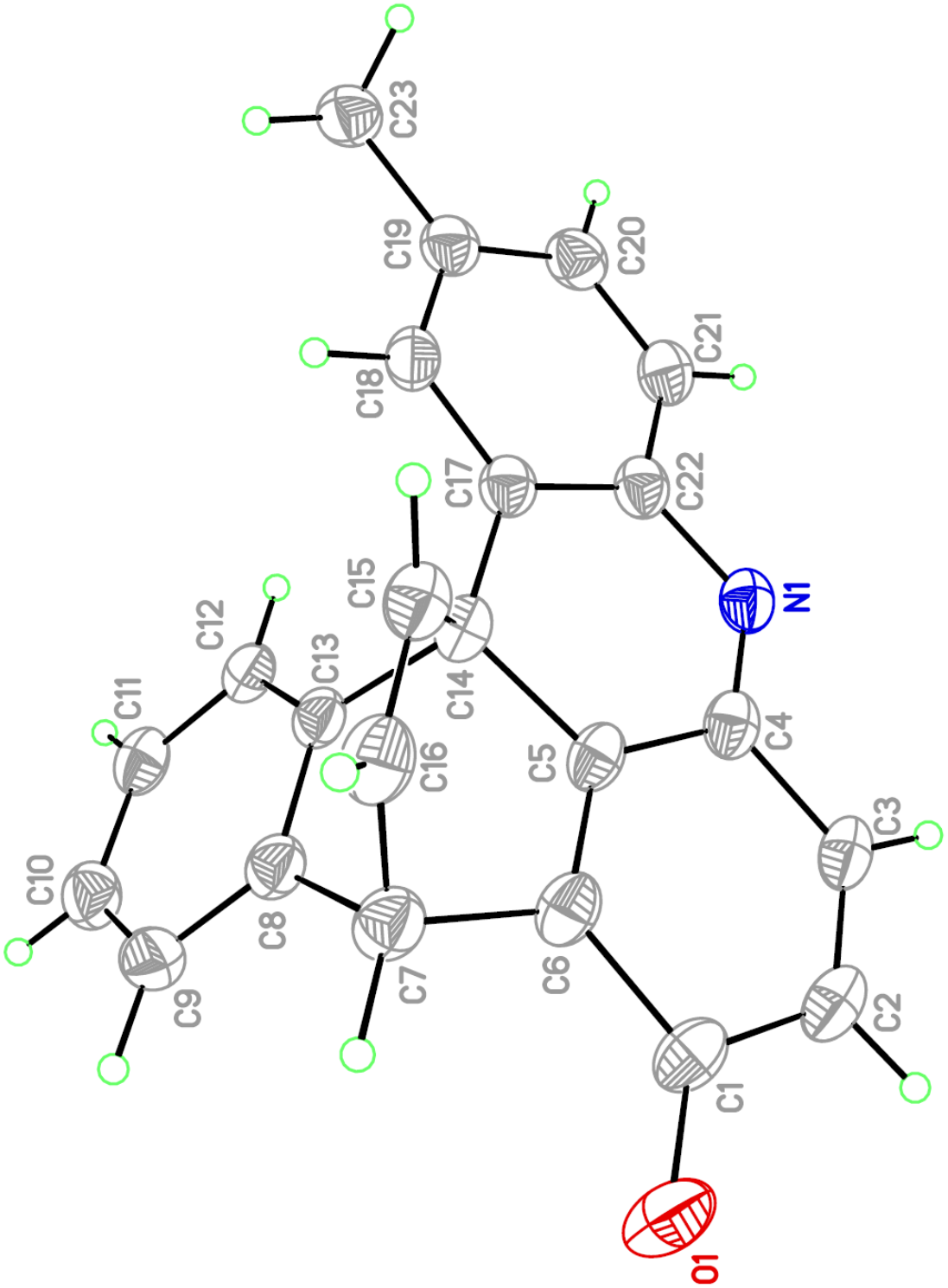


Table S2. Crystal data for compound **4d** (CCDC 1539212).

Empirical formula	C20 H13 N O3	
Formula weight	315.31	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 14.6184(7) Å	α= 90°.
	b = 4.0481(2) Å	β= 106.497(3)°.
	c = 25.0668(12) Å	γ = 90°.
Volume	1422.31(12) $Å^3$	
Z	4	
Density (calculated)	1.473 Mg/m^3	
Absorption coefficient	0.100 mm^{-1}	
F(000)	656	
Crystal size	0.20 x 0.08 x 0.03 mm^3	
Theta range for data collection	1.453 to 26.401°.	
Index ranges	-18<=h<=18, -4<=k<=5, -31<=l<=31	
Reflections collected	9794	
Independent reflections	2875 [R(int) = 0.0335]	
Completeness to theta = 25.242°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9485 and 0.8360	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2875 / 0 / 218	
Goodness-of-fit on F^2	1.102	
Final R indices [I>2sigma(I)]	R1 = 0.0408, wR2 = 0.1237	
R indices (all data)	R1 = 0.0561, wR2 = 0.1561	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.328 and -0.219 $e.Å^{-3}$	

Figure S64. Solid state structure of compound **4d.**

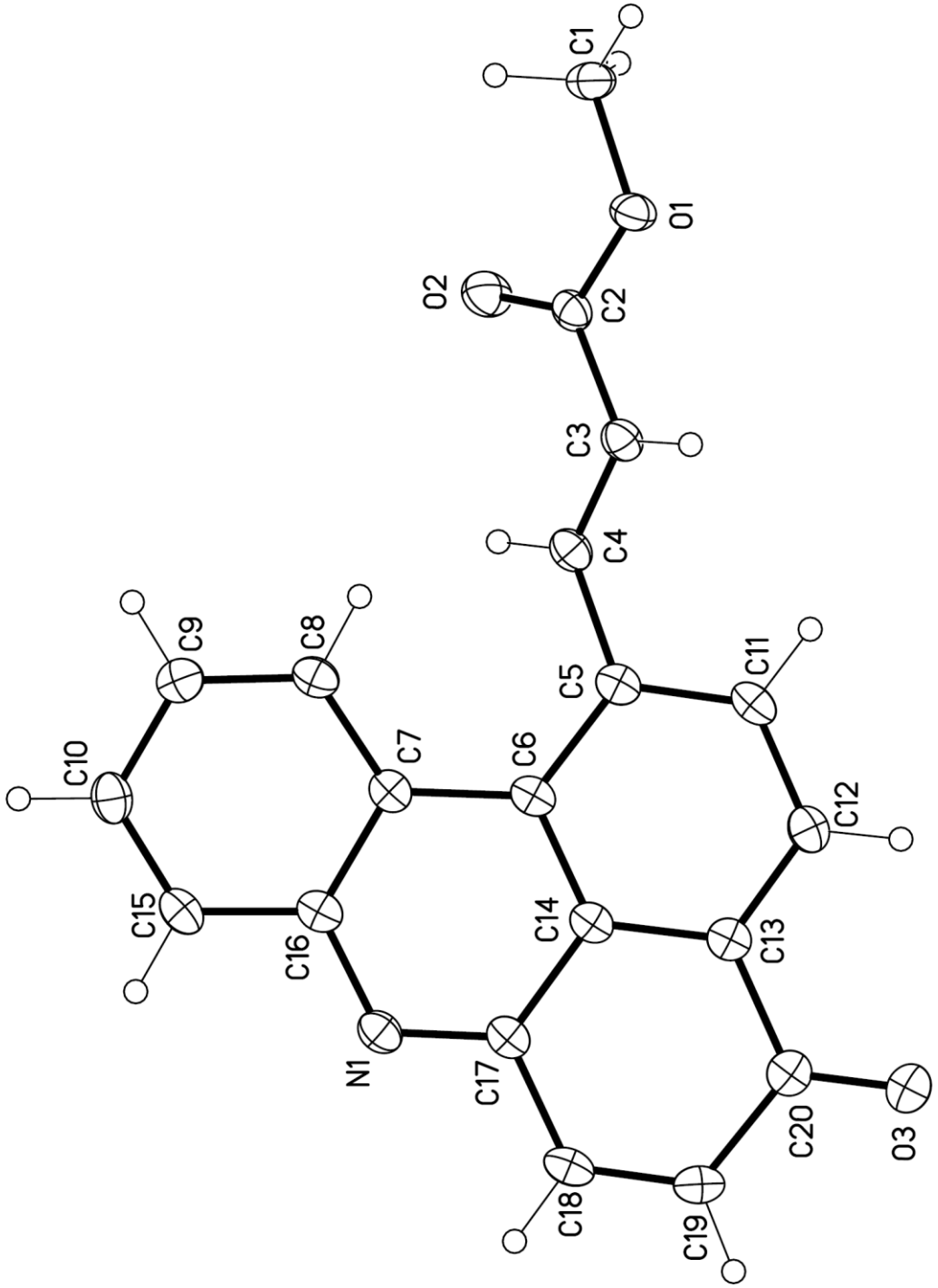


Table S3. Crystal data for compound **3k** (CCDC 1549537).

Empirical formula	C24 H17 N O	
Formula weight	335.38	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 9.1739(16) Å	α= 90°.
	b = 17.244(3) Å	β= 99.975(4)°.
	c = 11.0176(19) Å	γ = 90°.
Volume	1716.6(5) $Å^3$	
Z	4	
Density (calculated)	1.298 Mg/m^3	
Absorption coefficient	0.079 mm^{-1}	
F(000)	704	
Crystal size	0.12 x 0.10 x 0.04 mm^3	
Theta range for data collection	2.218 to 26.637°.	
Index ranges	-11<=h<=9, -21<=k<=21, -13<=l<=13	
Reflections collected	12729	
Independent reflections	3587 [R(int) = 0.0449]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9485 and 0.8333	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3587 / 0 / 237	
Goodness-of-fit on F^2	1.002	
Final R indices [I>2sigma(I)]	R1 = 0.0496, wR2 = 0.1118	
R indices (all data)	R1 = 0.0837, wR2 = 0.1276	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.553 and -0.272 $e.Å^{-3}$	

Figure S65. Solid state structure of compound **3k.**

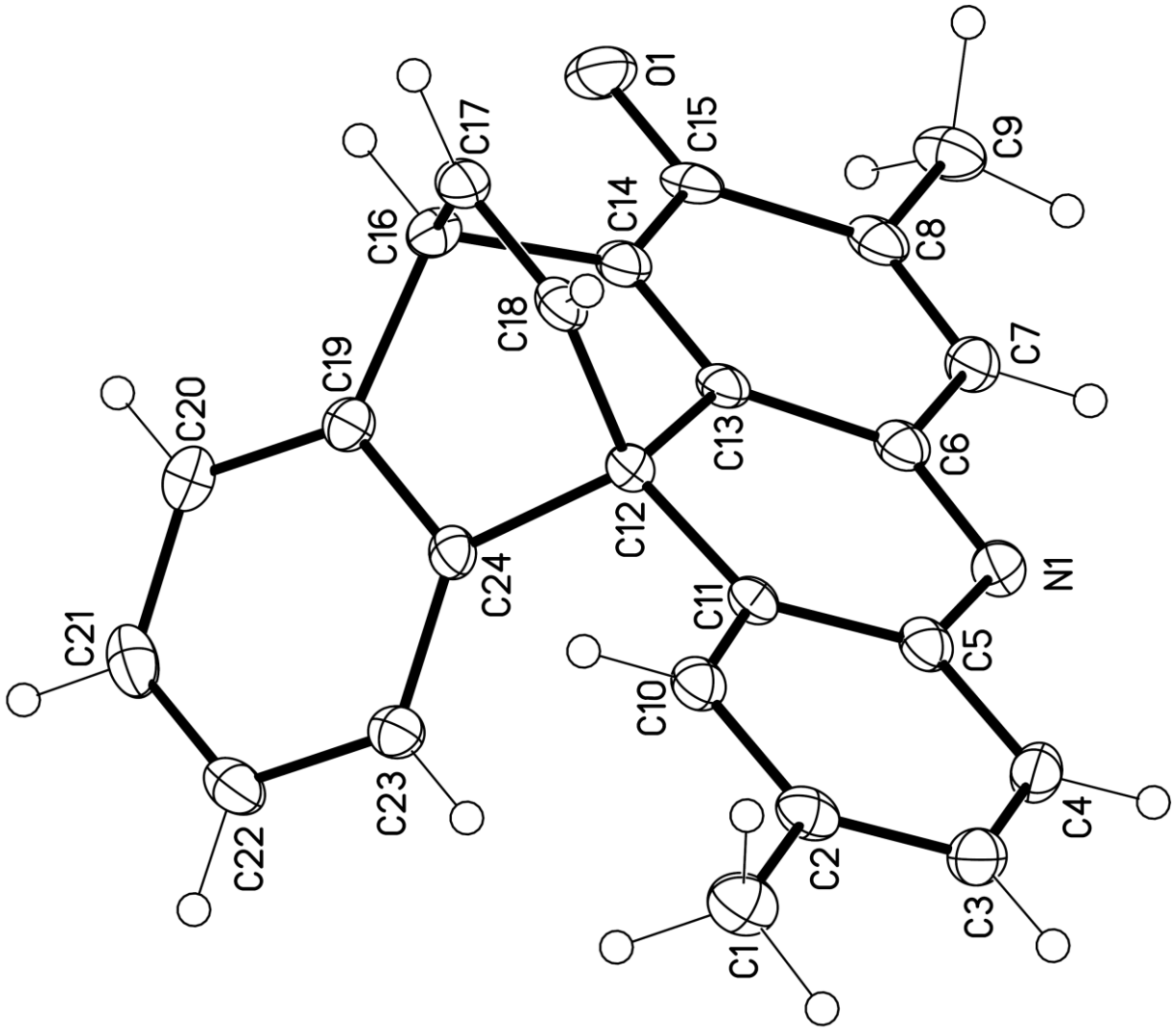


Figure S66. 2D-HSQC spectrum of compound **3m** ($CDCl_3$, 700 MHz)

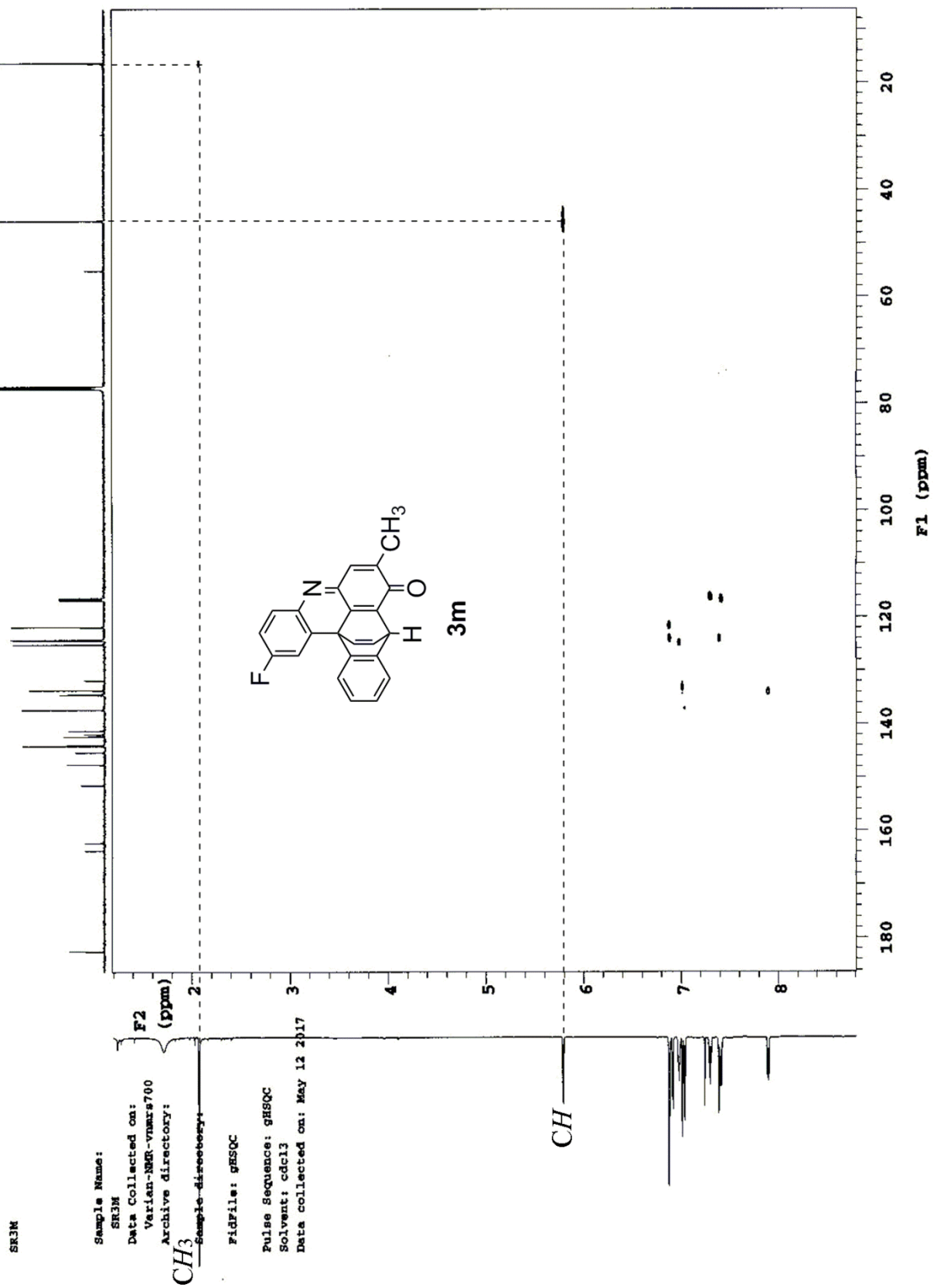


Figure S67. 2D-HMBC spectrum of compound **3m** ($CDCl_3$, 700 MHz)