Supporting Information

Indium-Catalyzed Formal [4+1+1]/[4+1] Isocyanide-Based Annulation for Construction of Polyfunctionalized Pyrano- and Furoquinolines

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Supporting Information

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1. General Considerations

Solvents, reagents, and catalysts were purchased from commercial suppliers and used without further purification. Solvents employed for column chromatography and work-up were purchased in an analytically pure grade and used without further purification.

TLC (Thin Layer Chromatography) was performed on silica gel pre-coated aluminum plates (Merck, 60 F-254) and was visualized by UV lamp (λ=254 nm).

Flash Column Chromatography was performed using a normal phase silica column packed with silica gel 60, (230-400 mesh) from Macherey-Nagel GmbH&Co.

NMR (Nuclear Magnetic Resonance) spectra were recorded using the Bruker Avance 400 spectrometer (400 MHz and 101 MHz for ^{1}H and ^{13}C, respectively) and/or on a Bruker DRX 500 (500 MHz and 126 MHz for ^{1}H and ^{13}C, respectively). Chemical shifts (δ) are given in ppm, relative to the signals for $CDCl_3$ (^{1}H NMR: δ= 7.27 ppm, ^{13}C NMR: δ= 77.00 ppm) and DMSO-*d6* (^{1}H NMR: *δ*= 2.50 ppm, ^{13}C NMR: *δ*= 39.5 ppm) and DMF (^{1}H NMR: δ= 8.01, 2.91, 2.74 ppm, ^{13}C NMR: δ= 162.69, 35.20, 30.08 ppm). Coupling constants (J) are reported in Hertz. Multiplicities for ^{1}H NMR are stated as follows: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad (br).

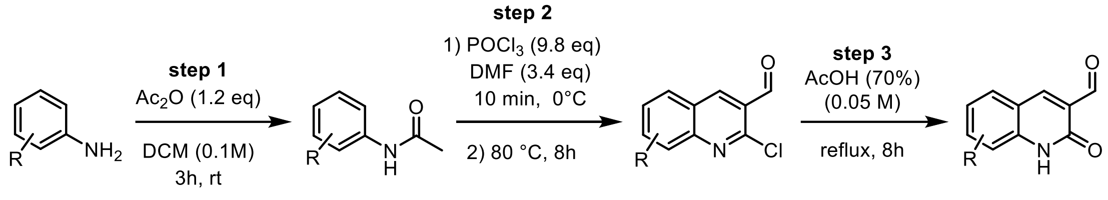
HR-MS (High-Resolution Mass Spectra) were recorded using a THERMO SCIENTIFIC Advantage, a THERMO SCIENTIFIC Executive instrument, and a Waters LCT Premier XE™ TOF (Time of Flight) mass spectrometer.

X-ray crystal data were collected on a Bruker APEX-II Quazar area detector. dichloromethane and methanol were used as the solvent at room temperature for crystal preparation.

The **fluorescence emission** and **UV–Visible absorption** spectra were recorded using a Varian Cary Eclipse fluorescence spectrophotometer (Cary 100, Australia) and a Varian UV–Visible spectrophotometer (Cary 100 Bio, Australia).

2. Experimental Procedures

2.1. General procedures for the synthesis of quinolones 1a-j.

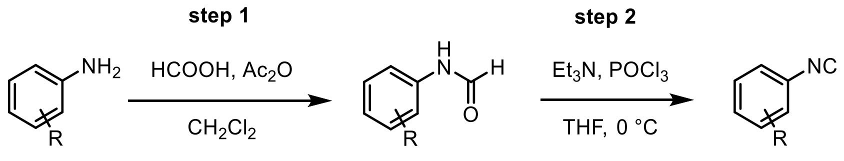


Step 1: In a 500 ml round bottom flask, aniline derivatives (50 mmol, 1.0 equiv) were dissolved in 200 ml of dichloromethane under an argon atmosphere. Then, acetic anhydride (60 mmol, 1.2 equiv) was added dropwise, and the reaction was stirred at room temperature till complete consumption of aniline derivatives. After completion of the reaction, the mixture was washed with a saturated solution of sodium bicarbonate, the organic layer dried with Na_2SO_4, and the solvent was removed under reduced pressure to obtain the desired acetanilides **S1a-j** in quantitative yield.

Step 2: Phosphoryl chloride (22.9 ml, 245 mmol) was added dropwise at 0°C to dimethylformamide (6.6 ml, 85 mmol) under nitrogen gas, then the acetanilides derivatives (25 mmol) were added at room temperature. The mixture was stirred for 8 hours at 85 °C, then slowly poured on crushed ice, filtered, and dried to obtain the desider compounds **S2a-j**.

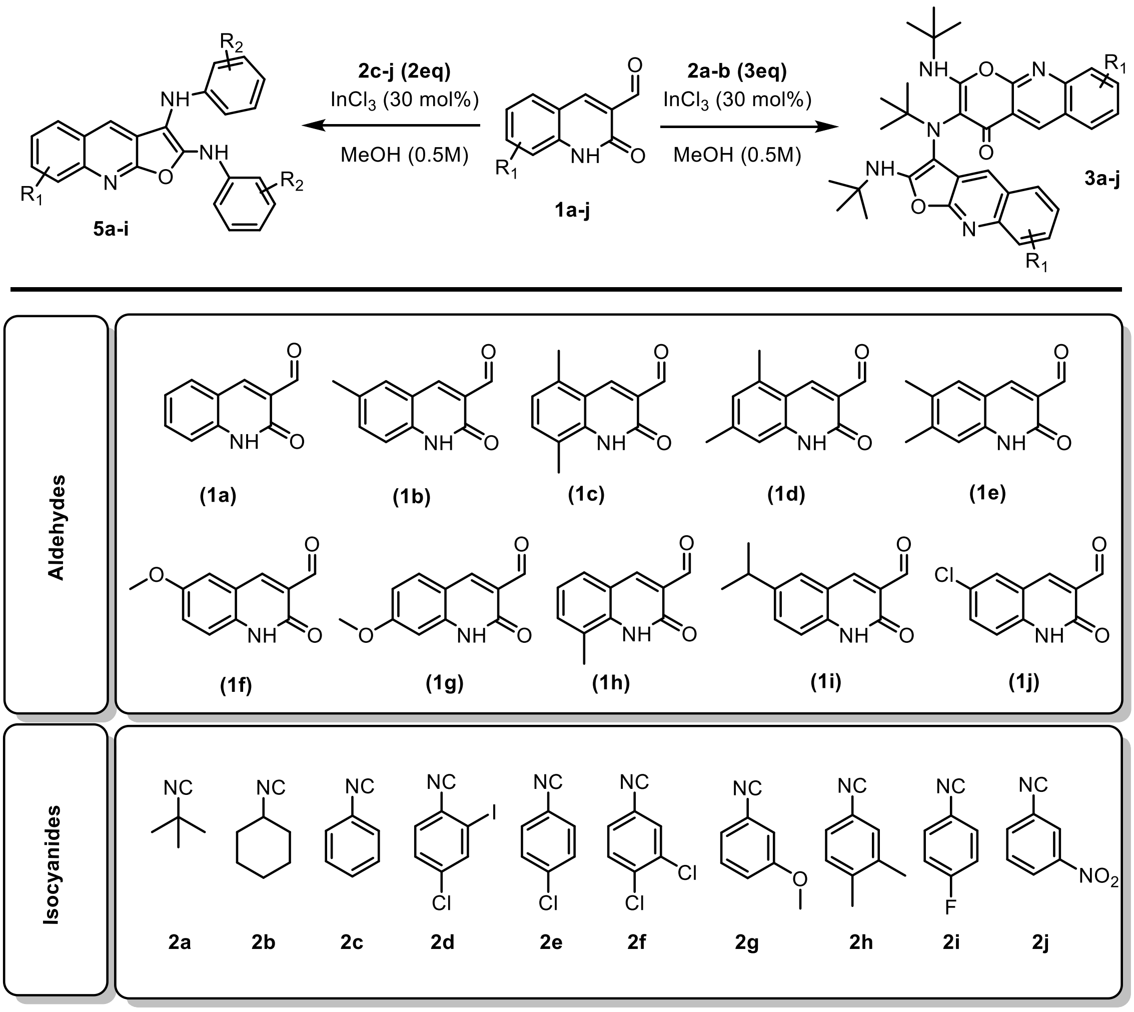
Step 3: 2-chloro-quinoline-3-carbaldahyde derivatives (10 mmol) were treated with 70% acetic acid aqueous solution (200 ml) at 95 °C for 6 hours and then the solution was cooled to room temperature to offer needle crystals of quinolones **1a-j**.[S1]

2.2. General procedures for the synthesis of 2c-j.



To formic acid (1.32 ml, 35 mmol), acetic anhydride (1.18 ml, 12.5 mmol) was added, and the mixture was stirred at room temperature. After stirring for 15 min, the mixture was added to the solution of aniline derivatives (1.21 g, 10.0 mmol) in CH_2Cl_2 (8 ml), and the mixture was stirred at room temperature. After stirring for 2h, the mixture was concentrated under reduced pressure to give formanilides. To the solution of the formanilide and Et_3N (4.04 ml, 29 mmol) in THF (20 ml) was added $POCl_3$ (1.07 ml, 11.56 mmol) at 0 °C and stirred at the same temperature. After stirring for 2h, the reaction mixture was basified with a saturated aqueous solution of $NaHCO_3$ and extracted with Et_2O. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The obtained residue was purified by silica gel column chromatography.[S2]

2.3 General procedures for the synthesis of 3a-j and 5a-i.



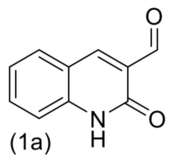
Route 1: To a solution of aldehydes **1a-j** (1 mmol) in methanol (0.5 M) were added Indium (III) chloride (30 mol%) and *t*-butyl isocyanides (1.5 mmol) and stirred overnight at 35 °C. After completion of the reaction, the solvent is concentrated under reduced pressure. The obtained residue was purified by silica gel flash column chromatography.

Route 2: To a solution of aldehydes **1a-j** (1 mmol) in methanol (0.5 M) were added Indium (III) chloride (30 mol%) and isocyanide derivatives **2c-j** (2 mmol) and stirred overnight at 35 °C. After completion of the reaction, the solid was filtered and washed with cold methanol to give pure **5a-i**.

3. Compounds Characterization Data

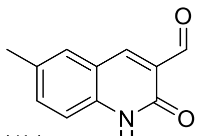
3.1 2-Oxo-1,2-dihydroquinoline-3-carbaldehyde derivatives (1a-j)

2-Oxo-1,2-dihydroquinoline-3-carbaldehyde (1a)


(1a)

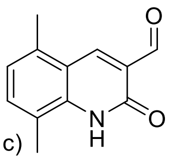
Pale yellow crystal (1402 mg, yield 81%); R_f = 0.33 (40:60 ethyl acetate/hexane); **^{1}H-NMR** (500 MHz, DMF-d7) δH= 12.06 (s, 1H), 10.34 (s, 1H), 8.51 (s, 1H), 8.02 (s, 1H), 7.97 (dd, J = 8.0, 1.4 Hz, 1H), 7.72 – 7.68 (m, 1H), 7.52 – 7.49 (m, 1H), 7.31 – 7.27 (m, 1H) ppm. **^{13}C-NMR** (126 MHz, DMF) δ= 190.2, 162.3, 142.8, 142.4, 134.3, 131.6, 126.8, 123.3, 119.1, 116.2 ppm. **HRMS-ESI** (m/z): calculated for $C_{10}H_6NO_3$ [M-H+O]$^-$ 188.0353 found 188.0353.

6-Methyl-2-oxo-1,2-dihydroquinoline-3-carbaldehyde (1b)


(1b)

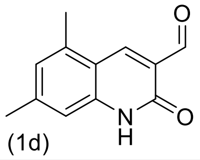
Lemon crystal (1590 mg, Yield 85%); R_f = 0.40 (40:60 ethyl acetate/hexane); **^{1}H-NMR** (500 MHz, DMSO-d_6) δ= 12.01 (s, 1H), 10.23 (s, 1H), 8.36 (s, 1zH), 7.65 (s, 1H), 7.46 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.26 (d, *J* = 8.4 Hz, 1H), 2.33 (s, 3H) ppm. **^{13}C-NMR** (126 MHz, DMSO) δ= 189.3, 160.9, 141.6, 139.0, 134.6, 131.4, 129.5, 125.5, 117.8, 115.0, 19.8 ppm. **HRMS-ESI** (m/z): calculated for $C_{11}H_9O_2$ NNa [M+Na]$^+$ 210.0525 found 210.0524.

5,8-Dimethyl-2-oxo-1,2-dihydroquinoline-3-carbaldehyde (1c)


(1c)

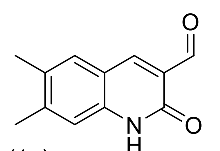
Dark yellow crystal (1187 mg, Yield 59%); R_f = 0.30 (40:60 ethyl acetate/hexane); **^{1}H-NMR** (500 MHz, DMSO-d_6) δ= 10.97 (s, 1H), 10.29 – 10.25 (m, 1H), 8.50 (d, *J* = 5.3 Hz, 1H), 7.37 (dd, *J* = 7.5, 3.3 Hz, 1H), 7.00 (dd, *J* = 7.5, 3.3 Hz, 1H), 2.54 (d, *J* = 2.9 Hz, 1H), 2.41 (d, *J* = 2.3 Hz, 1H) ppm. **^{13}C-NMR** (126 MHz, DMSO) δ= 189.2, 160.9, 142.0, 139.8, 139.0, 135.8, 134.4, 124.3, 123.2, 116.7, 17.6, 16.4 ppm. **HRMS-ESI** (m/z): calculated for $C_{12}H_{11}O_2$ NNa [M+Na]$^+$ 224.0682 found 224.0679.

5,7-Dimethyl-2-oxo-1,2-dihydroquinoline-3-carbaldehyde (1d)


(1d)

Yellow crystal (1247 mg, Yield 62%); R_f = 0.30 (40:60 ethyl acetate/hexane); **^{1}H-NMR** (500 MHz, DMSO-d_6) δ= 11.81 – 11.77 (m, 1H), 10.21 (s, 1H), 8.30 (s, 1H), 7.57 (s, 1H), 7.13 (d, *J* = 1.0 Hz, 1H), 2.32 (d, *J* = 1 Hz, 1H), 2.25 (d, *J* = 0.7 Hz, 1H) ppm. **^{13}C-NMR** (126 MHz, DMSO) δ= 189.2, 161.0, 143.7, 141.4, 139.5, 131.0, 129.9, 124.6, 116.1, 115.3, 19.8, 18.2 ppm. **HRMS-ESI** (m/z): calculated for $C_{12}H_{11}O_2$ NNa [M+Na]$^+$ 224.0682 found 224.0681.

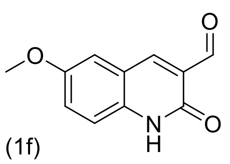
6,7-Dimethyl-2-oxo-1,2-dihydroquinoline-3-carbaldehyde (1e)



(1e)

Yellow green crystal (1629 mg, Yield 81%); R_f = 0.24 (40:60 ethyl acetate/hexane); **^{1}H-NMR** (500 MHz, DMSO-*d*$_6$) δ= 12.05 (s, 1H), 10.20 (s, 1H), 8.35 (s, 1H), 7.61 (s, 1H), 7.11 (s, 1H), 2.30 (s, 3H), 2.24 (s, 3H) ppm. **^{13}C-NMR** (126 MHz, DMSO) δ= 189.7, 161.5, 144.3, 141.8, 139.8, 131.5, 130.3, 124.6, 116.4, 115.6, 20.3, 18.7 ppm. **HRMS-ESI** (m/z): calculated $C_{12}H_{11}O_2$ NNa $[M+Na]^+$ 224.0682 found 224.0679.

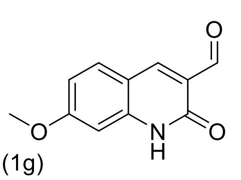
6-Methoxy-2-oxo-1,2-dihydroquinoline-3-carbaldehyde (1f)



(1f)

Olive crystal (1665 mg, Yield 82%, 5.0 mmol scale); R_f = 0.35 (40:60 ethyl acetate/hexane); **^{1}H-NMR** (400 MHz, DMSO-d6) δ= 12.09 (s, 1H), 10.22 (s, 1H), 8.40 (d, J = 0.5 Hz, 1H), 7.42 – 7.41 (m, 1H), 7.28 – 7.27 (m, 1H), 3.78 (s, 3H) ppm. **^{13}C-NMR** (101 MHz, DMSO) δ= 189.8, 161.0, 154.4, 141.6, 135.9, 125.7, 123.5, 118.6, 116.7, 111.1, 55.5 ppm. **HRMS-ESI** (m/z): calculated for $C_{11}H_9O_3$NNa $M+Na]^+$ 226.0475 found 226.0472.

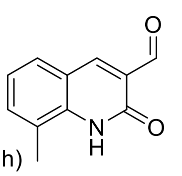
7-Methoxy-2-oxo-1,2-dihydroquinoline-3-carbaldehyde (1g)



(1g)

Khaki crystal (1584 mg, Yield 78%); R_f = 0.25 (15:85 ethyl acetate/hexane); **^{1}H-NMR** (400 MHz, DMSO-*d*$_6$) δ= 12.03 (s, 1H), 10.16 (s, 1H), 8.40 (s, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 6.86 (dd, *J* = 8.8, 2.1 Hz, 1H), 6.81 (d, *J* = 2.1 Hz, 1H), 3.84 (s, 1H) ppm. **^{13}C-NMR** (101 MHz, DMSO) δ= 189.2, 163.8, 161.7, 143.5, 142.2, 132.6, 122.5, 112.5, 112.4, 97.7, 55.6 ppm. **HRMS-ESI** (m/z): calculated for $C_{11}H_9O_3$NNa $M+Na]^+$ 226.0475 found 226.0474.

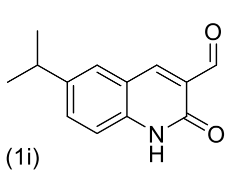
8-Methyl-2-oxo-1,2-dihydroquinoline-3-carbaldehyde (1h)



(1h)

Yellow crystal (1552 mg, Yield 83%); R_f = 0.23 (15:85 ethyl acetate/hexane); **^{1}H-NMR** (400 MHz, DMSO-*d*$_6$) δ= 11.35 (s, 1H), 10.25 (s, 1H), 8.48 (s, 1H), 7.79 – 7.72 (m, 1H), 7.51 – 7.47 (m, 1H), 7.18 – 7.13 (m, 1H), 2.44 (d, *J* = 0.8 Hz, 1H) ppm. **^{13}C-NMR** (101 MHz, DMSO) δ= 189.6, 161.8, 142.9, 139.5, 134.7, 129.0, 125.3, 123.9, 122.4, 118.2, 17.1 ppm. **HRMS-ESI** (m/z): calculated for $C_{11}H_9O_2$ NNa $[M+Na]^+$ 210.0525 found 210.0526.

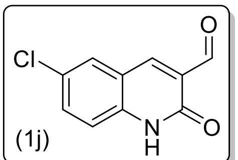
6-Isopropyl-2-oxo-1,2-dihydroquinoline-3-carbaldehyde (1i)



(1i)

lemon crystal (1334 mg, Yield 62%); R_f = 0.20 (15:85 ethyl acetate/hexane); **^{1}H-NMR** (500 MHz, DMSO-*d*$_6$) δ= 12.34 (s, 1H), 10.22 (s, 1H), 8.47 (s, 1H), 8.06 (d, *J* = 2.4 Hz, 1H), 7.68 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.35 (d, *J* = 8.9 Hz, 1H) ppm. **^{13}C-NMR** (101 MHz, DMSO) δ= 189.7, 161.3, 142.7, 142.2, 139.5, 132.7, 127.4, 125.4, 118.0, 115.4, 32.7, 23.6 ppm. **HRMS-ESI** (m/z): calculated for $C_{13}H_{14}O_2N$ $[M+H]^+$ 216.1019 found 216.1018.

6-Chloro-2-oxo-1,2-dihydroquinoline-3-carbaldehyde (1j)

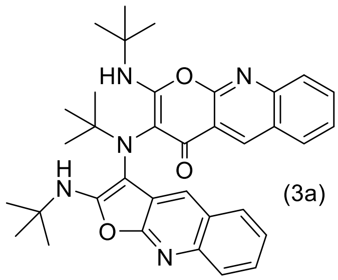


(1j)

lemone crystal (1847 mg, Yield 89%); R_f = 0.33 (15:85 ethyl acetate/hexane); **^{1}H-NMR** (500 MHz, DMSO-*d*$_6$) δ= 12.34 (s, 1H), 10.22 (s, 1H), 8.47 (s, 1H), 8.06 (d, *J* = 2.4 Hz, 1H), 7.68 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.35 (d, *J* = 8.9 Hz, 1H) ppm. **^{13}C-NMR** (126 MHz, DMSO) δ= 189.6, 161.2, 141.2, 139.8, 133.3, 129.5, 126.4, 126.3, 119.2, 117.3 ppm. **HRMS-ESI** (m/z): calculated for $C_{10}H_5O_2NCl$ $[M-H]^-$ 206.0014. found 206.0014.

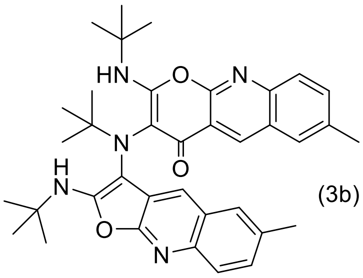
3.2 Furo- and pyranoquenoline derivatives (3a-j)

3-(*tert*-Butyl(2-(*tert*-butylamino)furo[2,3-*b*]quinolin-3-yl)amino)-2-(*tert*-butylamino)-4*H*-pyrano[2,3-*b*]quinolin-4-one (3a)


(3a)

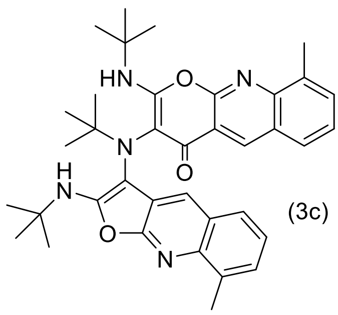
Red solid (173 mg, Yield 60 %); mp 285-287 °C; R_f = 0.15 (15:85 ethyl acetate/hexane); **^{1}H-NMR** (400 MHz, $CDCl_3$) : **δ_H =** 9.13 (s, 1H, H-4-quinoline), 8.38 (s, 1H, H-4-quinoline), 8.05 (dt, *J* = 9.4, 1.4 Hz, 2H, H-Ar), 7.99 (dd, *J* = 8.3, 1.4 Hz, 1H, H-Ar), 7.81 (dt, *J* = 8.5, 1.5 Hz, 1H, H-Ar), 7.71 (dd, *J* = 8.0, 1.6 Hz, 1H, H-Ar), 7.66 (s, 1H, -NH), 7.59 (dt, *J* = 8.1, 1.1 Hz, 1H, H-Ar), 7.48 (dt, *J* = 8.3, 1.6 Hz, 1H, H-Ar), 7.43 (dt, *J* = 8.2, 1.4 Hz, 1H, H-Ar), 7.37 (s, 1H, -NH), 1.65 (s, 9H, -*t*-Bu), 1.51 (s, 9H, -*t*-Bu), 1.46 (s, 9H, -*t*-Bu). **^{13}C-NMR** (101 MHz, $CDCl_3$) : **δ_C =** 173.9, 167.8, 161.0, 157.1, 154.4, 147.4, 140.6, 137.7, 131.9, 128.9, 128.1, 127.4, 127.0, 126.4, 126.2, 125.6, 125.4, 124.8, 118.4, 116.7, 109.8, 96.7, 96.1, 60.5, 54.3, 53.1, 30.4, 30.2, 30.1. **HRMS-ESI** (m/z): Calc. for $C_{35}H_{39}N_5NaO_3$ $[M+Na]^+$: 600.2945, found 600.2951.

3-(tert-Butyl(2-(*tert*-butylamino)-6-methylfuro[2,3-*b*]quinolin-3-yl)amino)-2-(*tert*-butylamino)-7-methyl-4*H*-pyrano[2,3-*b*]quinolin-4-one (3b)


(3b)

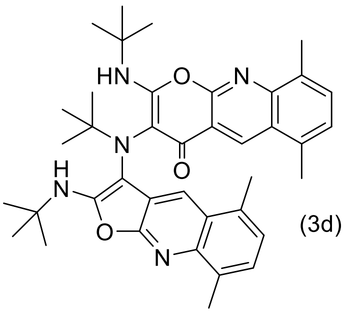
Red solid (166 mg, Yield 55 %); mp 275-277 °C; R_f = 0.18 (15:85 ethyl acetate/hexane); **^{1}H-NMR** (300 MHz, $CDCl_3$) : **δ_H =** 9.03 (d, *J* = 0.9 Hz, 1H, H-4-quinoline), 8.33 (s, 1H, H-4-quinoline), 7.95(d, *J* = 8.5 Hz, 1H, H-Ar), 7.87 (d, *J* = 8.5 Hz, 1H, H-Ar), 7.79 – 7.77 (m, 1H, H-Ar), 7.64 (dd, *J* = 8.8, 2.0 Hz, 1H, H-Ar), 7.58 (s, 1H, -NH), 7.48 – 7.45 (m, 1H, H-Ar), 7.34 (s, 1H, -NH), 7.31 (dd, *J* = 8.6, 1.9 Hz, 1H H-Ar), 2.56 (s, 3H, Me-Ar), 2.52 (s, 3H, Me-Ar), 1.65 (s, 9H, -*t*-Bu), 1.49 (s, 9H, -*t*-Bu), 1.45 (s, 9H, -*t*-Bu). **^{13}C-NMR** (75 MHz, $CDCl_3$) : **δ_C =** 174.0, 167.8, 160.8, 156.8, 154.0, 145.9, 139.0, 136.8, 136.4, 134.3, 134.3, 127.7, 127.7, 127.6, 127.4, 127.1, 126.1, 124.7, 118.3, 116.3, 109.8, 96.8, 60.4, 54.2, 53.0, 30.4, 30.3, 30.1, 21.6, 21.5. **HRMS-ESI** (m/z): calculated for $C_{37}H_{44}N_5O_3$ $[M+H]^+$: 606.3439, found 606.3445.

3-(*tert*-Butyl(2-(*tert*-butylamino)-8-methylfuro[2,3-*b*]quinolin-3-yl)amino)-2-(*ter*t-butylamino)-9-methyl-4*H*-pyrano[2,3-*b*]quinolin-4-one (3c)


(3c)

Red solid (196 mg, Yield 65 %); mp 270-275 °C; R_f = 0.34 (15:85 ethyl acetate/hexane); **^{1}H-NMR** (300 MHz, $CDCl_3$) : **δ_H =** 9.08 (s, 1H, H-4-quinoline), 8.30 (s, 1H, H-4-quinoline), 7.87 (d, *J* = 8.2 Hz, 1H, H-Ar), 7.66 (s, 1H, H-Ar), 7.63 (s, 1H, -NH), 7.58 (dd, *J* = 6.7, 2.7 Hz, 1H, H-Ar), 7.47 (t, *J* = 8.3 Hz, 1H, H-Ar), 7.35 (s, 1H, -NH), 7.34 – 7.31 (m, 2H, H-Ar) 2.81 (s, 3H, Me-Ar), 2.77 (s, 3H, Me-Ar), 1.64 (s, 9H, -*t*-Bu), 1.52 (s, 9H, -*t*-Bu), 1.46 (s, 9H, -*t*-Bu). **^{13}C-NMR** (75 MHz, $CDCl_3$) : **δ_C =** 174.2, 167.8, 161.0, 156.5, 153.5, 146.6, 139.9, 137.7, 136.4, 135.9, 131.7, 127.3, 127.1, 126.7, 126.1, 125.8, 124.3, 123.8, 118.0, 117.3, 109.8, 96.9, 60.4, 54.2, 53.0, 30.5, 30.2, 30.1, 18.5, 17.8. **HRMS-ESI** (m/z): Calc. for $C_{37}H_{42}N_5O_3$ $[M-H]^+$: 604.3295, found 6043290.

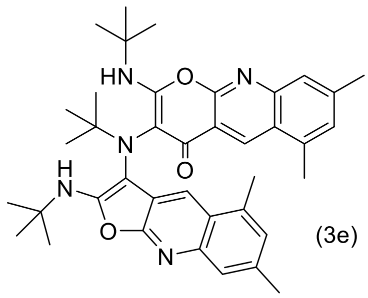
3-(*tert*-Butyl(2-(*tert*-butylamino)-5,8-dimethylfuro[2,3-*b*]quinolin-3-yl)amino)-2-(tert-butylamino)-6,9-dimethyl-4*H*-pyrano[2,3-*b*]quinolin-4-one (3d)



(3d)

Red solid (164 mg, Yield 52 %); mp 260-263 °C; R_f = 0.37 (15:85 ethyl acetate/hexane); **^{1}H-NMR** (300 MHz, $CDCl_3$) : **δ_H =** 9.27 (s, 1H, H-4-quinoline), 8.20 (s, 1H, H-4-quinoline), 7.86 (s, 1H, -NH), 7.53 (dd, *J* = 7.1, 1.1 Hz, 1H, H-Ar), 7.32 – 7.27 (m, 1H, H-Ar), 7.26 – 7.22 (m, 2H, , H-Ar), 7.20 – 7.16 (m, 1H, H-Ar), 2.78 (s, 6H, Me-Ar), 2.73 (s, 3H, Me-Ar), 2.68 (s, 3H, Me-Ar), 1.63 (s, 9H, -*t*-Bu), 1.51 (s, 9H, -*t*-Bu), 1.48 (s, 9H, -*t*-Bu). **^{13}C-NMR** (75 MHz, $CDCl_3$) : **δ_C =** 174.4, 167.7, 160.8, 156.1, 153.2, 147.1, 140.0, 134.3, 134.1, 134.0, 133.8, 131.5, 129.8, 126.8, 126.6, 126.4, 125.4, 125.1, 125.0, 117.2, 114.2, 109.8, 97.4, 60.7, 54.1, 53.0, 30.5, 30.4, 30.1, 19.5, 19.1, 18.5, 17.8. **HRMS-ESI** (m/z): Calc. for $C_{39}H_{47}N_5NaO_3$ $[M+Na]^+$: 656.3571, found 656.3578.

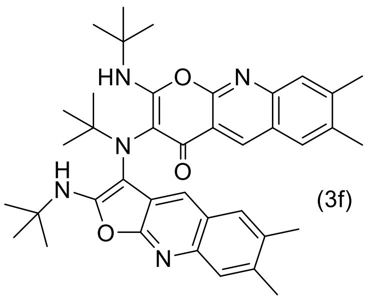
3-(*tert*-Butyl(2-(*tert*-butylamino)-5,7-dimethylfuro[2,3-*b*]quinolin-3-yl)amino)-2-(*tert*-butylamino)-6,8-dimethyl-4*H*-pyrano[2,3-*b*]quinolin-4-one (3e)



(3e)

Red solid (158 mg, Yield 50 %); mp 265-267 °C; R_f = 0.2 (15:85 ethyl acetate/hexane); **^{1}H-NMR** (300 MHz, $CDCl_3$) : **δ_H =** 9.23 (s, 1H, H-4-quinoline), 8.20 (s, 1H, H-4-quinoline), 7.80 (s, 1H, -NH), 7.69 (d, *J* = 1.8 Hz, 1H, H-Ar), 7.64 (d, *J* = 1.8 Hz, 1H, H-Ar), 7.25 (d, *J* = 2.0 Hz, 2H, H-Ar), 7.13 (s, 1H, -NH), 2.78 (s, 3H, Me-Ar), 2.67 (s, 3H, Me-Ar), 2.53 (s, 3H, Me-Ar), 2.49 (s, 3H, Me-Ar), 1.63 (s, 9H, -*t*-Bu), 1.49 (s, 9H, -*t*-Bu), 1.47 (s, 9H, -*t*-Bu). **^{13}C-NMR** (75 MHz, $CDCl_3$) : **δ_C =** 174.3, 167.6, 160.5, 156.9, 154.4, 148.3, 142.6, 141.2, 136.0, 134.9, 134.0, 131.7, 129.3, 127.8, 125.6, 125.2, 124.9, 124.6, 116.9, 113.9, 109.7, 97.2, 60.7, 54.1, 53.0, 30.4, 30.1, 22.1, 21.6, 19.5, 19.1. **HRMS-ESI** (m/z): calculated for $C_{39}H_{48}N_5O_3$ $[M+H]^+$: 634.3752, found 634.3759.

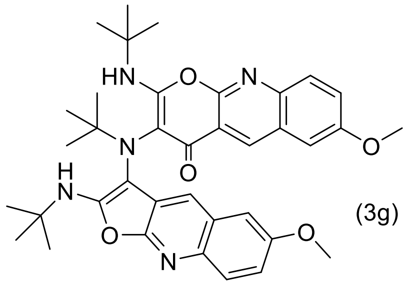
3-(*tert*-Butyl(2-(*tert*-butylamino)-6,7-dimethylfuro[2,3-*b*]quinolin-3-yl)amino)-2-(*tert*-butylamino)-7,8-dimethyl-4H-pyrano[2,3-*b*]quinolin-4-one (3f)



(3f)

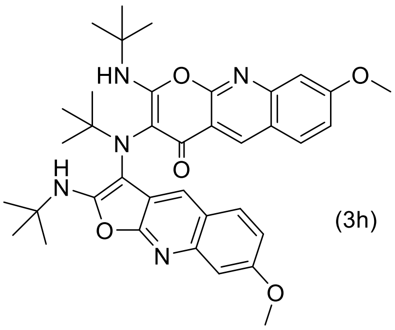
Red solid (183 mg, Yield 58 %); mp 263-266 °C; R_f = 0.2 (15:85 ethyl acetate/hexane); **^{1}H-NMR** (300 MHz, $CDCl_3$) : **δ_H =** 8.98 (s, 1H, H-4-quinoline), 8.23 (s, 1H, H-4-quinoline), 7.82 (s, 1H, -NH), 7.75 – 7.72 (m, 2H, H-Ar), 7.57 (s, 1H, H-Ar), 7.45 (s, 1H, H-Ar) 7.30 (s, 1H, -NH), 2.48 (s, 3H, Me-Ar), 2.45 (s, 3H, Me-Ar), 2.43 (s, 6H, Me-Ar), 1.63 (s, 9H, -*t*-Bu), 1.48 (s, 9H, -*t*-Bu), 1.44 (s, 9H, -*t*-Bu). **^{13}C-NMR** (75 MHz, $CDCl_3$) : **δ_C =** 174.2, 167.7, 160.5, 156.8, 154.2, 146.5, 143.0, 139.7, 136.5, 136.4, 135.2, 134.2, 127.9, 127.6, 127.3, 125.8, 125.7, 125.4, 125.2, 117.6, 116.4, 109.7, 97.0, 60.3, 54.1, 53.0, 30.4, 30.3, 30.1, 20.8, 20.3, 20.1, 20.0. **HRMS-ESI** (m/z): calculated for $C_{39}H_{48}N_5O_3$ $[M+H]^+$: 634.3752, found 634.3762.

3-(*tert*-Butyl(2-(*tert*-butylamino)-6-methoxyfuro[2,3-*b*]quinolin-3-yl)amino)-2-(*tert*-butylamino)-7-methoxy-4H-pyrano[2,3-*b*]quinolin-4-one (3g)


(3g)

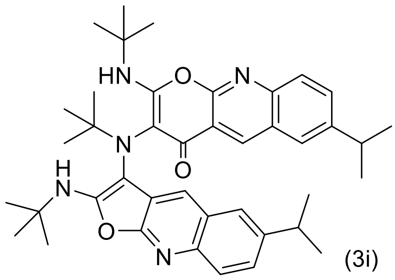
Red solid (175 mg, Yield 55 %); mp 288-290 °C; R_f = 0.08 (15:85 ethyl acetate/hexane); **^{1}H-NMR** (300 MHz, $CDCl_3$) : **δ_H =** 9.01 (d, *J* = 0.8 Hz, 1H, H-4-quinoline), 8.15 (s, 1H, H-4-quinoline), 7.89 (d, *J* = 9.1 Hz, 1H, H-Ar), 7.63 (d, *J* = 0.8 Hz, 1H, H-Ar), 7.60 (d, *J* = 9.0 Hz, 1H, H-Ar), 7.36 (dd, *J* = 8.9, 2.4 Hz, 2H, H-Ar), 7.24 (d, *J* = 5.4 Hz 1H, H-Ar), 7.22 (dd, , *J* = 8.9 Hz, 2.4 Hz, 1H, H-Ar), 7.11 (dd, *J* = 8.9, 2.6 Hz, 1H, H-Ar), 3.96 (s, 3H, CH_3-O), 3.92 (s, 3H, CH_3-O), 1.62 (s, 9H, -*t*-Bu), 1.48 (s, 9H, -*t*-Bu), 1.44 (s, 9H, -*t*-Bu). **^{13}C-NMR** (75 MHz, $CDCl_3$) : **δ_C =** 174.3, 167.4, 162.9, 160.0, 158.0, 157.5, 155.0, 149.6, 142.1, 137.2, 130.0, 126.7, 124.2, 122.4, 122.2, 120.2, 117.6, 117.3, 116.0, 109.7, 107.1, 105.9, 96.9, 60.3, 55.8, 55.4, 54.1, 53.0, 30.4, 30.3, 30.1. **HRMS-ESI** (m/z): calculated for $C_{37}H_{44}N_5O_5$ $[M+H]^+$: 638.3337, found 638.3340.

3-(*tert*-Butyl(2-(*tert*-butylamino)-7-methoxyfuro[2,3-*b*]quinolin-3-yl)amino)-2-(*tert*-butylamino)-8-methoxy-4H-pyrano[2,3-*b*]quinolin-4-one (3h)


(3h)

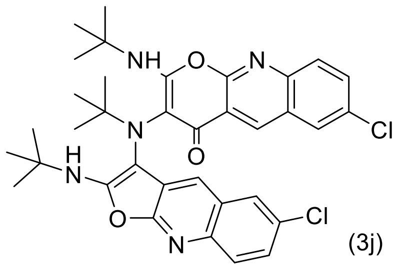
Red solid (168 mg, Yield 53 %); mp 285-288 °C; R_f = 0.08 (15:85 ethyl acetate/hexane); **^{1}H-NMR** (300 MHz, $CDCl_3$) : **δ_H =** 8.99 (s, 1H, H-4-quinoline), 8.35 (s, 1H, H-4-quinoline), 7.96 (d, *J* = 9.3 Hz, 1H, 1H, H-Ar), 7.88 (d, *J* = 9.0 Hz, 1H, 1H, H-Ar), 7.55 (s, 1H, -NH), 7.46 (dd, *J* = 9.3, 2.8 Hz, 1H, H-Ar), 7.31 (s, 1H, -NH), 7.25 (d, *J* = 2.8 Hz, 1H, H-Ar), 7.15 (dd, *J* = 9.1, 2.8 Hz, 1H, H-Ar), 7.01 (d, *J* = 2.8 Hz, 1H, H-Ar), 3.96 (s, 3H, CH_3-O), 3.93 (s, 3H, CH_3-O), 1.64 (s, 9H, -*t*-Bu), 1.50 (s, 9H, -*t*-Bu), 1.45 (s, 9H, -*t*-Bu). **^{13}C-NMR** (75 MHz, $CDCl_3$) : **δ_C =** 174.0, 167.7, 161.0, 157.7, 156.8, 156.0, 153.1, 143.4, 136.1, 135.9, 129.4, 129.3, 128.2, 128.1, 126.4, 125.2, 118.4, 116.8, 115.8, 109.9, 105.6, 104.7, 96.9, 60.4, 55.6, 55.5, 54.2, 53.0, 30.4, 30.2, 30.1. **HRMS-ESI** (m/z): calculated for $C_{37}H_{44}N_5O_5$ $[M+H]^+$: 638.3337, found 638.3339.

3-(*tert*-Butyl(2-(*tert*-butylamino)-6-isopropylfuro[2,3-*b*]quinolin-3-yl)amino)-2-(*tert*-butylamino)-7-isopropyl-4*H*-pyrano[2,3-*b*]quinolin-4-one (3i)


(3i)

Red solid (211 mg, Yield 64 %); mp 266-270 °C; R_f = 0.19 (15:85 ethyl acetate/hexane); **^{1}H-NMR** (300 MHz, $CDCl_3$) : **δ_H =** 9.07 (d, *J* = 0.8 Hz, 1H), 8.33 (s, 1H, H-4-quinoline), 8.00 (d, *J* = 8.8 Hz, 1H, H-4-quinoline), 8.00 (d, *J* = 8.8 Hz, 1H, H-Ar), 7.92 (d, *J* = 8.6 Hz, 1H, H-Ar), 7.81 (d, *J* = 2.0 Hz, 1H, H-Ar), 7.72 (dd, *J* = 8.9, 2.0 Hz, 1H, H-Ar), 7.62 (s, 1H, -NH), 7.49 (d, *J* = 2.0 Hz, 1H, H-Ar), 7.40 (dd, *J* = 8.7, 2.0 Hz, 1H, H-Ar), 7.35 (s, 1H, -NH), 3.11 (m, 2H, -CH-Ar), 1.65 (s, 9H, -*t*-Bu), 1.50 (s, 9H, -*t*-Bu), 1.46 (s, 9H, -*t*-Bu), 1.38 – 1.37 (m, 6H, Me-CH), 1.36 – 1.34(m, 6H, Me-CH). **^{13}C-NMR** (75 MHz, $CDCl_3$) : **δ_C =** 174.1, 167.8, 160.8, 156.9, 154.1, 147.1, 146.2, 145.2, 139.4, 137.2, 132.0, 127.9, 127.4, 127.1, 126.1, 125.0, 124.9, 122.0, 118.3, 116.7, 109.8, 96.9, 60.4, 54.2, 53.0, 34.1, 34.0, 30.4, 30.3, 30.1, 24.1, 24.1, 23.8, 23.7. **HRMS-ESI** (m/z): Calc. for $C_{41}H_{50}N_5O_3$ $[M-H]^+$: 660.3925, found 660.3919.

3-(*tert*-Butyl(2-(*tert*-butylamino)-6-chlorofuro[2,3-*b*]quinolin-3-yl)amino)-2-(*tert*-butylamino)-7-chloro-4*H*-pyrano[2,3-*b*]quinolin-4-one (3j)

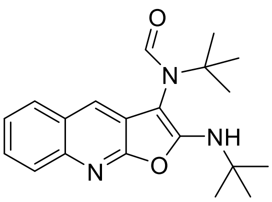


(3j)

Red solid (230 mg, Yield 63 %); mp 285-287 °C; R_f = 0.2 (15:85 ethyl acetate/hexane); **^{1}H-NMR** (300 MHz, $CDCl_3$) : **δ_H =** 9.03 (s, 1H, H-4-quinoline), 8.50 (s, 1H, H-4-quinoline), 8.02 – 7.99 (m, 2H, H-Ar), 7.89 (d, *J* = 8.9 Hz, 1H, H-Ar), 7.73 (dd, *J* = 9.0, 2.3 Hz, 1H, H-Ar), 7.65 (d, *J* = 2.3 Hz, 1H, H-Ar) 7.51 (s, 1H, -NH), 7.39 (dd, *J* = 9.0, 2.3 Hz, 1H, H-Ar), 7.34 (s, 1H, -NH), 1.65 (s, 9H, -*t*-Bu), 1.51 (s, 9H, -*t*-Bu), 1.44 (s, 9H, -*t*-Bu). **^{13}C-NMR** (75 MHz, $CDCl_3$) : **δ_C =** 173.5, 167.8, 161.5, 157.2, 154.5, 145.7, 138.8, 136.7, 132.8, 132.3, 130.3, 129.7, 129.5, 128.3, 127.5, 127.3, 127.0, 125.8, 124.1, 119.1, 115.1, 109.9, 96.6, 60.6, 54.5, 53.2, 30.3, 30.3, 30.1. **HRMS-ESI** (m/z): calculated for $C_{35}H_{37}N_5O_3Cl_2$ $[M-H]^+$: 644.2215, found 644.2202.

3.3 Furo quinoline derivatives (4a-b)

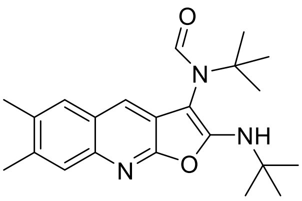
***N*-*tert*-Butyl-*N*-(2-(*tert*-butylamino)furo[2,3-*b*]quinolin-3-yl)formamide (4a)**



(4a)

Pale yellow solid, (152 mg, 45 % yield); m.p. 250-254 °C. R_f = 0.36 (50:50 ethyl acetate/hexane); **^{1}H NMR** (300 MHz, $CDCl_3$) : **δ_H =** 9.06 (s, 1H, H-4-quinoline), 8.10 – 8.05 (m, 1H, H-Ar), 8.04 – 7.98 (m, 1H, H-Ar), 7.80 (ddd, *J* = 8.6, 6.9, 1.5 Hz, 1H, H-Ar), 7.57 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H, H-Ar), 6.70 (brs, 1H, -NH), 3.76 (s, 1H, -CH-CO), 1.62 (s, 9H, -t-Bu), 1.21 (s, 9H, -t-Bu). **^{13}C NMR** (75 MHz, $CDCl_3$) : **δ_C =** 171.8, 164.9, 155.3, 147.1, 137.3, 131.5, 128.9, 127.9, 126.2, 118.8, 105.1, 63.8, 55.7, 53.3, 30.2, 30.1. **HRMS-ESI** (m/z): calculated for $C_{20}H_{24}N_3O_2$ $[M-H]^-$: 338.1874, found 338.1880.

***N*-*tert*-Butyl-*N*-(2-(*tert*-butylamino)-6,7-dimethylfuro[2,3-*b*]quinolin-3-yl)formamide (4b)**

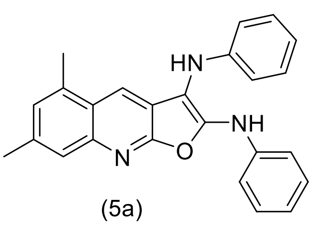


(4b)

Pale yellow solid, (238 mg, 65 % yield) m.p. 245-249 °C. R_f = 0.4 (50:50 ethyl acetate/hexane); **^{1}H NMR** (300 MHz, $CDCl_3$): **δ_H =** 8.92 (s, 1H, H-4-quinoline), 7.83 (s, 1H, H-Ar), 7.71 (s, 1H, H-Ar), 6.63 (brs, 1H, -NH), 3.76 (s, 3H, Me-Ar), 2.48 (s, 3H, Me-Ar), 2.45 (s, 1H, -CH-CO), 1.60 (s, 9H, -t-Bu), 1.20 (s, 9H, -t-Bu). **^{13}C NMR** (75 MHz, $CDCl_3$) : **δ_C =** 172.2, 164.8, 154.7, 146.3, 142.5, 136.0, 127.9, 127.3, 125.7, 117.4, 105.0, 63.9, 55.6, 53.1, 30.2, 30.1, 20.7, 19.9. . **HRMS-ESI** (m/z): calculated for $C_{22}H_{30}N_3O_2$ $[M-H]^+$: 368.2333, found 368.2329.

3.4 Furo quinoline derivatives (5a-i)

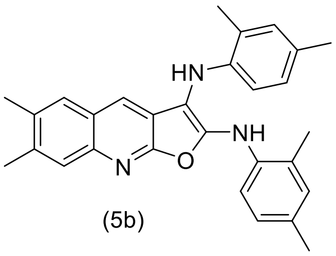
5,7-Dimethyl-*N*2,*N*3-diphenylfuro[2,3-*b*]quinoline-2,3-diamine (5a)



(5a)

Orange solid (46 mg, Yield 20%); mp 205-207 °C; R_f = 0.18 (15:85 ethyl acetate/hexane); **^{1}H-NMR** (499 MHz, DMSO-d_6) δ 9.38 (s, 1H), 7.80 (s, 1H), 7.57 (s, 1H), 7.36 (s, 1H), 7.27-7.18 (m, 4H), 7.17 (s, 1H), 7.10 (t, *J* = 7.7 Hz, 2H), 6.90 (t, *J* = 7.1 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 2H), 6.64 (t, *J* = 7.3 Hz, 1H), 2.52 (s, 3H), 2.44 (s, 3H) ppm. **^{13}C-NMR** (126 MHz, DMSO) δ 156.9, 149.3, 146.0, 142.4, 140.2, 136.1, 132.4, 129.4, 127.6, 125.5, 124.3, 123.3, 121.4, 120.1, 119.0, 117.7, 117.7, 113.8, 99.6, 21.7, 16.6. **HRMS-ESI** (m/z): calculated for $C_{25}H_{22}N_3O$ $[M+H]^+$ 380.1757 found 380.1830.

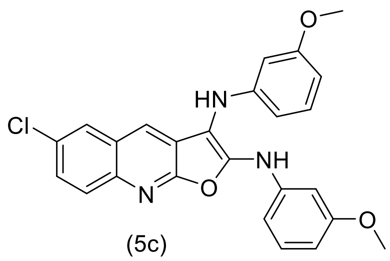
_N_2,_N_3-Bis(2,4-dimethylphenyl)-6,7-dimethylfuro[2,3-_b_]quinoline-2,3-diamine (5b)



(5b)

Brown solid (46 mg, Yield 10%); mp 210-212 °C; R_f = 0.35 (15:85 ethyl acetate/hexane); **^{1}H-NMR** (400 MHz, DMSO-d_6) δ 9.15 (s, 1H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.63 (s, 1H), 7.04 – 6.90 (m, 4H), 6.86 (d, *J* = 8.1 Hz, 1H), 6.50 (d, *J* = 2.7 Hz, 1H), 6.39 (dd, *J* = 8.1, 2.5 Hz, 1H), 2.41 (s, 3H), 2.36 (s, 3H), 2.15 (s, 3H), 2.11 (s, 3H), 2.09 (s, 3H), 2.07 (s, 3H) ppm. **^{13}C-NMR** (101 MHz, DMSO) δ 156.8, 149.8, 145.0, 141.5, 138.7, 137.1, 137.0, 136.8, 134.5, 130.4, 130.3, 129.1, 127.4, 126.9, 125.7, 124.9, 121.4, 121.2, 119.2, 115.4, 115.3, 111.2, 98.8, 20.4, 20.2, 20.0, 20.0, 19.1, 18.9. **HRMS-ESI** (m/z): calculated for$C_{29}H_{30}N_3O$ $[M+H]^+$ 436.2382 found 436.2383.

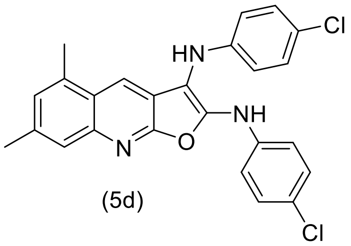
6-Chloro-_N_2,_N_3-bis(3-methoxyphenyl)furo[2,3-_b_]quinoline-2,3-diamine (5c)



(5c)

Yellow-green solid (99 mg, Yield 21%); mp 158-160 °C; R_f = 0.20 (15:85 ethyl acetate/hexane);**^{1}H-NMR** (400 MHz, DMSO-d_6) δ 9.63 (s, 1H), 8.12 (d, *J* = 2.5 Hz, 1H), 7.94 (d, *J* = 9.0 Hz, 1H), 7.85 (s, 1H), 7.58 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.37 (s, 1H), 7.19 (t, *J* = 8.2 Hz, 1H), 7.07 – 6.98 (m, 1H), 6.89 (ddd, *J* = 8.1, 2.1, 0.9 Hz, 1H), 6.84 (t, *J* = 2.3 Hz, 1H), 6.54 (ddd, *J* = 8.3, 2.5, 0.9 Hz, 1H), 6.31 – 6.24 (m, 3H), 3.66 (s, 3H), 3.62 (s, 3H) ppm. **^{13}C-NMR** (101 MHz, DMSO) δ 160.9, 160.4, 157.3, 151.0, 148.3, 141.6, 140.8, 133.8, 130.3, 130.2, 130.0, 129.6, 128.1, 127.7, 126.3, 122.8, 121.4, 110.6, 107.7, 106.7, 103.9, 103.4, 99.5, 98.2, 55.3, 55.2 ppm. **HRMS-ESI** (m/z): calculated for $C_{25}H_{21}ClN_3O_3$ $[M+H]^+$ 446.1266 found 446.1268.

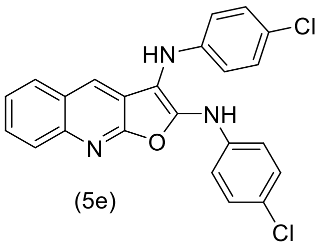
_N_2,_N_3-Bis(4-chlorophenyl)-5,7-dimethylfuro[2,3-_b_]quinoline-2,3-diamine (5d)



(5d)

lemon solid (207 mg, Yield 44%); mp 210-213 °C; R_f = 0.28 (15:85 ethyl acetate/hexane); **^{1}H-NMR** (400 MHz, DMSO-d_6) δ 9.59 (s, 1H), 7.85 (s, 1H), 7.62 (s, 1H), 7.59 (s, 1H), 7.33 – 7.27 (m, 2H), 7.25 – 7.18 (m, 3H), 7.14 (d, *J* = 8.8 Hz, 1H), 6.68 (d, *J* = 8.8 Hz, 1H), 2.57 (s, 3H), 2.47 (s, 3H) ppm. **^{13}C-NMR** (101 MHz, DMSO) δ 156.8, 148.7, 145.7, 143.4, 139.8, 137.1, 133.7, 129.2, 129.1, 128.2, 125.5, 125.0, 124.4, 121.1, 120.2, 119.3, 119.2, 115.3, 99.5, 21.7, 19.4 ppm. **HRMS-ESI** (m/z): calculated for $C_{25}H_{20}Cl_2N_3O$ $[M+H]^+$ 448.0978 found 448.0974.

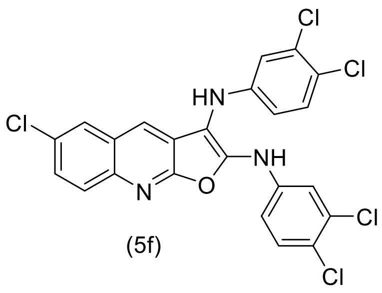
_N_2,_N_3-Bis(4-chlorophenyl)furo[2,3-_b_]quinoline-2,3-diamine (5e)



(5e)

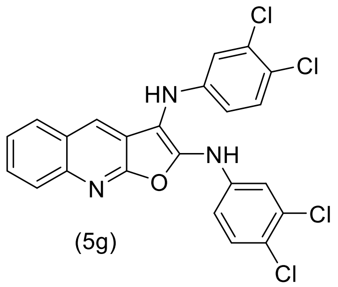
Dark yellow solid (111 mg, Yield 25%); mp 211-213 °C; R_f = 0.20 (15:85 ethyl acetate/hexane); **^{1}H-NMR** (400 MHz, DMSO-d_6) δ 9.72 (s, 1H), 8.03 – 7.96 (m, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.87 (s, 1H), 7.61 (ddd, *J* = 8.5, 6.8, 1.5 Hz, 1H), 7.57 (s, 1H), 7.51 – 7.46 (m, 1H), 7.35 – 7.23 (m, 4H), 7.18 – 7.11 (m, 2H), 6.74 – 6.64 (m, 2H) ppm. **^{13}C-NMR** (101 MHz, DMSO) δ 157.0, 150.0, 146.0, 142.6, 139.6, 129.5, 129.3, 129.2, 128.1, 127.9, 127.7, 127.2, 126.0, 125.4, 125.3, 122.7, 121.4, 121.1, 120.7, 119.5, 115.2, 98.4 ppm. **HRMS-ESI** (m/z): calculated for $C_{23}H_{16}Cl_2N_3O$ $[M+H]^+$ 420.0665 found 420.0666.

6-Chloro-*N*2,*N*3-bis(3,4-dichlorophenyl)furo[2,3-*b*]quinoline-2,3-diamine (5f)


(5f)

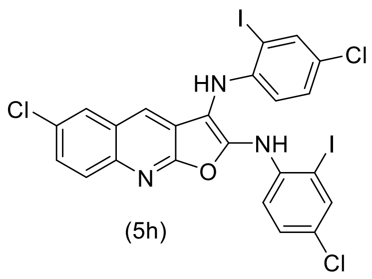
Cream solid (389 mg, Yield 71%); mp 215-218 °C; R_f = 0.35 (15:85 ethyl acetate/hexane); **^{1}H-NMR** (400 MHz, DMSO-d_6) δ 9.39 (s, 1H), 8.13 (d, *J* = 2.4 Hz, 1H), 7.95 (d, *J* = 9.2 Hz, 2H), 7.62 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.57 (d, *J* = 2.3 Hz, 1H), 7.43 (d, *J* = 2.4 Hz, 1H), 7.35 – 7.28 (m, 3H), 7.09 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.58 (d, *J* = 8.8 Hz, 1H). **^{13}C-NMR** (101 MHz, DMSO) δ 157.2, 149.8, 141.3, 141.2, 136.1, 130.1, 129.7, 129.4, 128.9, 128.2, 128.2, 128.0, 127.5, 126.5, 125.3, 123.5, 122.6, 122.2, 121.5, 119.5, 115.5, 99.5. **HRMS-ESI** (m/z): calculated for $C_{23}H_{13}Cl_5N_3O$ $[M+H]^+$ 521.9495 found 521.9496.

***N*2,*N*3-Bis(3,4-dichlorophenyl)furo[2,3-*b*]quinoline-2,3-diamine (5g)**


(5g)

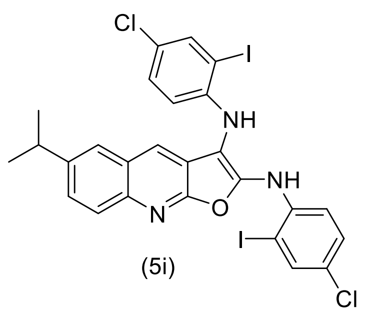
Yellow solid (328 mg, Yield 64%); mp 205-208 °C; R_f = 0.27 (15:85 ethyl acetate/hexane); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.24 (s, 1H), 8.01 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.98 (s, 1H), 7.95 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.64 (ddd, *J* = 8.4, 6.8, 1.5 Hz, 1H), 7.58 – 7.54 (m, 1H), 7.50 (ddd, *J* = 8.4, 6.8, 1.5 Hz, 1H), 7.44 (d, *J* = 2.4 Hz, 1H), 7.37 (s, 1H), 7.30 (m, 2H), 7.09 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.60 (d, *J* = 8.8 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, DMSO) δ 157.1, 148.7, 143.0, 141.3, 136.6, 129.3, 128.9, 128.2, 128.2, 128.2, 128.1, 127.1, 126.9, 125.4, 124.6, 123.9, 122.7, 121.5, 121.1, 119.6, 115.6, 100.5 ppm. **HRMS-ESI** (m/z): calculated for $C_{23}H_{14}Cl_4N_3O$ $[M+H]^+$ 487.9884 found 487.9885.

6-Chloro-*N*2,*N*3-bis(4-chloro-2-iodophenyl)furo[2,3-*b*]quinoline-2,3-diamine (5h)


(5h)

Pale brown solid (446 mg, Yield 61%); mp 210-212 °C; R_f = 0.33 (15:85 ethyl acetate/hexane); **^{1}H-NMR** (400 MHz, DMSO-d_6) δ 9.28 (s, 1H), 8.11 (d, *J* = 2.4 Hz, 1H), 7.93 (d, *J* = 9.0 Hz, 1H), 7.87 (s, 1H), 7.85 (d, *J* = 2.4 Hz, 1H), 7.69 (d, *J* = 2.5 Hz, 1H), 7.60 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.34 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.25 (d, *J* = 8.6 Hz, 1H), 7.12 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.50 (s, 1H), 6.48 (d, *J* = 8.8 Hz, 1H) ppm. **^{13}C-NMR** (101 MHz, DMSO) δ 157.2, 151.2, 145.1, 140.9, 140.2, 138.3, 137.8, 130.0, 129.7, 129.3, 129.1, 128.1, 127.9, 126.4, 124.8, 122.7, 122.3, 121.7, 114.7, 98.3, 94.5, 85.0. **HRMS-ESI** (m/z): calculated for $C_{23}H_{13}Cl_3I_2N_3O$ $[M+H]^+$ 705.8208 found 705.8209.

***N*2,*N*3-Bis(4-chloro-2-iodophenyl)-6-isopropylfuro[2,3-*b*]quinoline-2,3-diamine (5i)**


(5i)

Sand solid (458 mg, Yield 62%); mp 160-162 °C; R_f = 0.30 (15:85 ethyl acetate/hexane); **^{1}H-NMR** (400 MHz, DMSO-d_6) δ 9.01 (s, 1H), 7.87 – 7.83 (m, 2H), 7.82 – 7.78 (m, 2H), 7.72 (d, *J* = 2.4 Hz, 1H), 7.55 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.34 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.21 (d, *J* = 8.7 Hz, 1H), 7.12 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.60 (s, 1H), 6.48 (d, *J* = 8.8 Hz, 1H), 3.04 (hept, *J* = 6.9 Hz, 1H), 1.27 (d, *J* = 6.9 Hz, 6H) ppm. **^{13}C-NMR** (101 MHz, DMSO) δ 156.8, 149.7, 145.4, 145.1, 141.6, 140.8, 138.3, 137.9, 129.3, 128.3, 127.9, 127.7, 127.1, 124.1, 123.6, 123.0, 122.3, 121.1, 114.9, 100.0, 93.2, 85.1, 33.8, 24.3 ppm. **HRMS-ESI** (m/z): calculated for $C_{26}H_{20}Cl_2I_2N_3O$ $[M+H]^+$ 713.9067 found 713.9063.

4. Absorption and Emission Data

4.1 Absorption and Emission of Compound 5a in n-Hexane

Table S1. Photophysical properties of compound **5a** recorded in **n-Hexane**

Compound	$\lambda_{max,abs}$ [nm][a]	$\lambda_{max,em}$ [nm][b]	Stokes shift [nm]
5a	350	476	126

[a]Recorded in n-Hexane, T = 293 K, c =6.5×10^{-5} M. [b]Recorded in n-Hexane, T = 293 K, c=6.5×10^{-6} M.

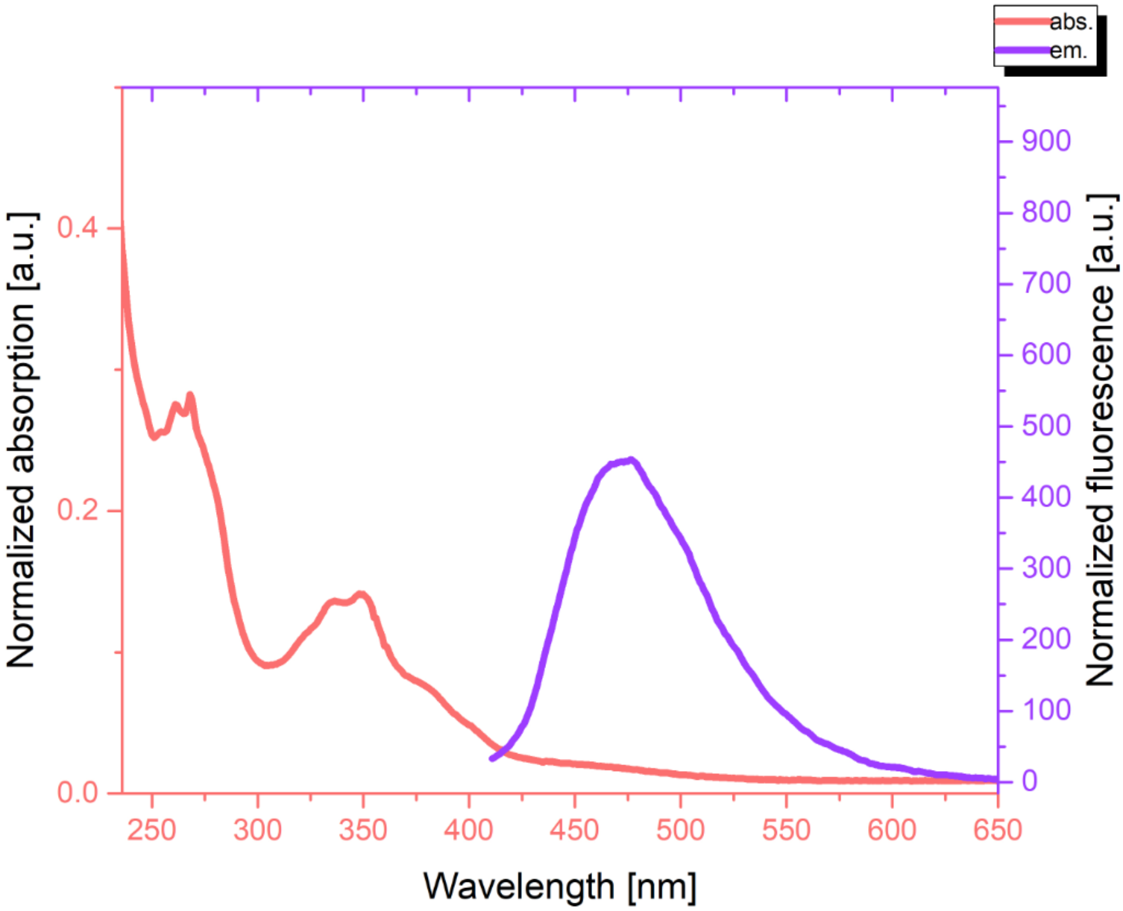


Figure S1. Normalized absorption and emission spectra for compound **5a** in **n-Hexane** (T = 293 °C, λ_{exc} = 365 nm).

4.2 Absorption and Emission of Compound 5a in Toluene

Table S2. Photophysical properties of compound **5a** recorded in **Toluene**

Compound	$\lambda_{max,abs}$ [nm][a]	$\lambda_{max,em}$ [nm][b]	Stokes shift [nm]
5a	354	499	145

[a]Recorded in Toluene, *T* = 293 K, *c* =6.5×10^{-5} M. [b]Recorded in Toluene, *T* = 293 K, *c*=6.5×10^{-6} M.

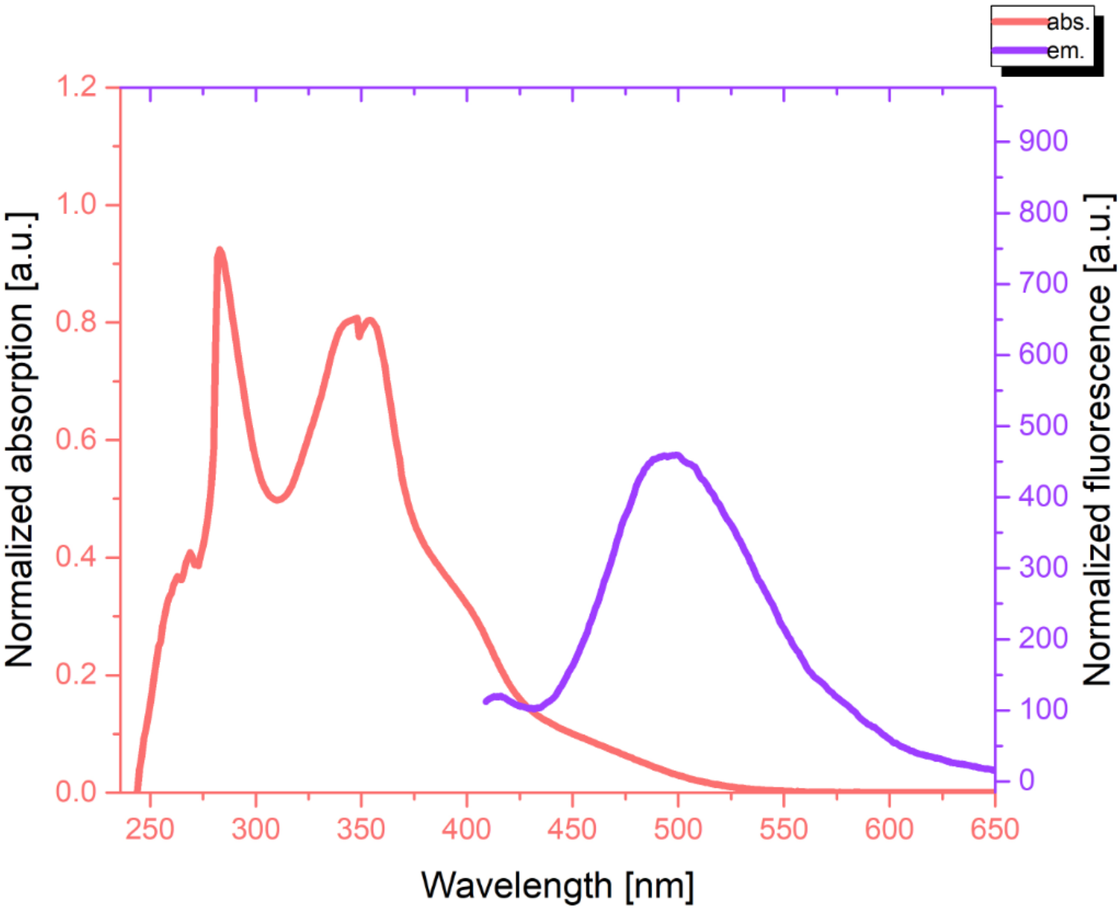


Figure S2. Normalized absorption and emission spectra for compound **5a** in **Toluene** (T = 293 °C, λ_{exc} = 365 nm).

4.3 Absorption and Emission of Compound 5a in DCM

Table S3. Photophysical properties of compound **5a** recorded in **DCM**

Compound	$\lambda_{max,abs}$ [nm][a]	$\lambda_{max,em}$ [nm][b]	Stokes shift [nm]
5a	349	574	225

[a]Recorded in DCM, *T* = 293 K, *c* =6.5×10^{-5} M. [b]Recorded in DCM, *T* = 293 K, *c*=6.5×10^{-6} M.

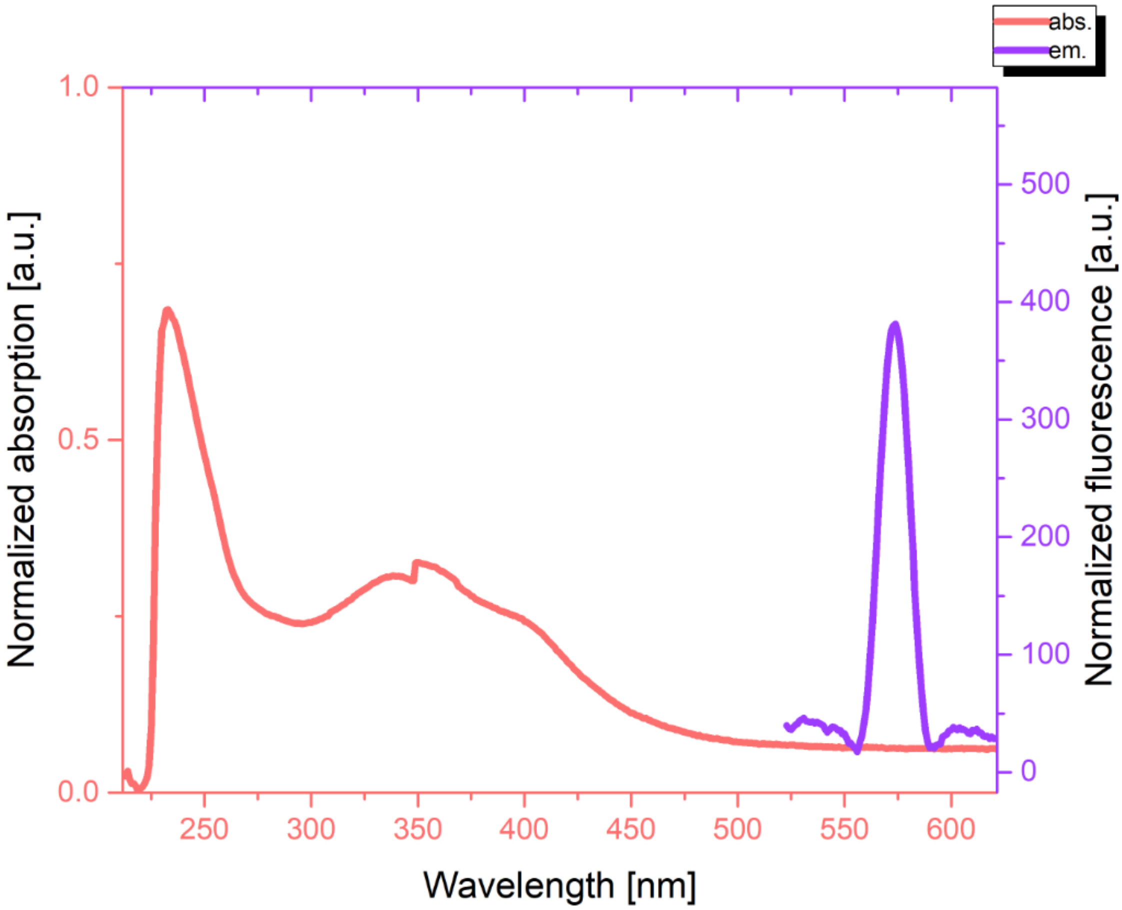


Figure S3. Normalized absorption and emission spectra for compound **5a** in **DCM** (T = 293 °C, λ_{exc} = 365 nm).

4.4 Absorption and Emission of Compound 5a in THF

Table S4. Photophysical properties of compound **5a** recorded in **THF**

Compound	$\lambda_{max,abs}$ [nm][a]	$\lambda_{max,em}$ [nm][b]	Stokes shift [nm]
5a	378	526	148

[a]Recorded in THF, T = 293 K, c =6.5×10^{-5} M. [b]Recorded in THF, T = 293 K, c=6.5×10^{-6} M.

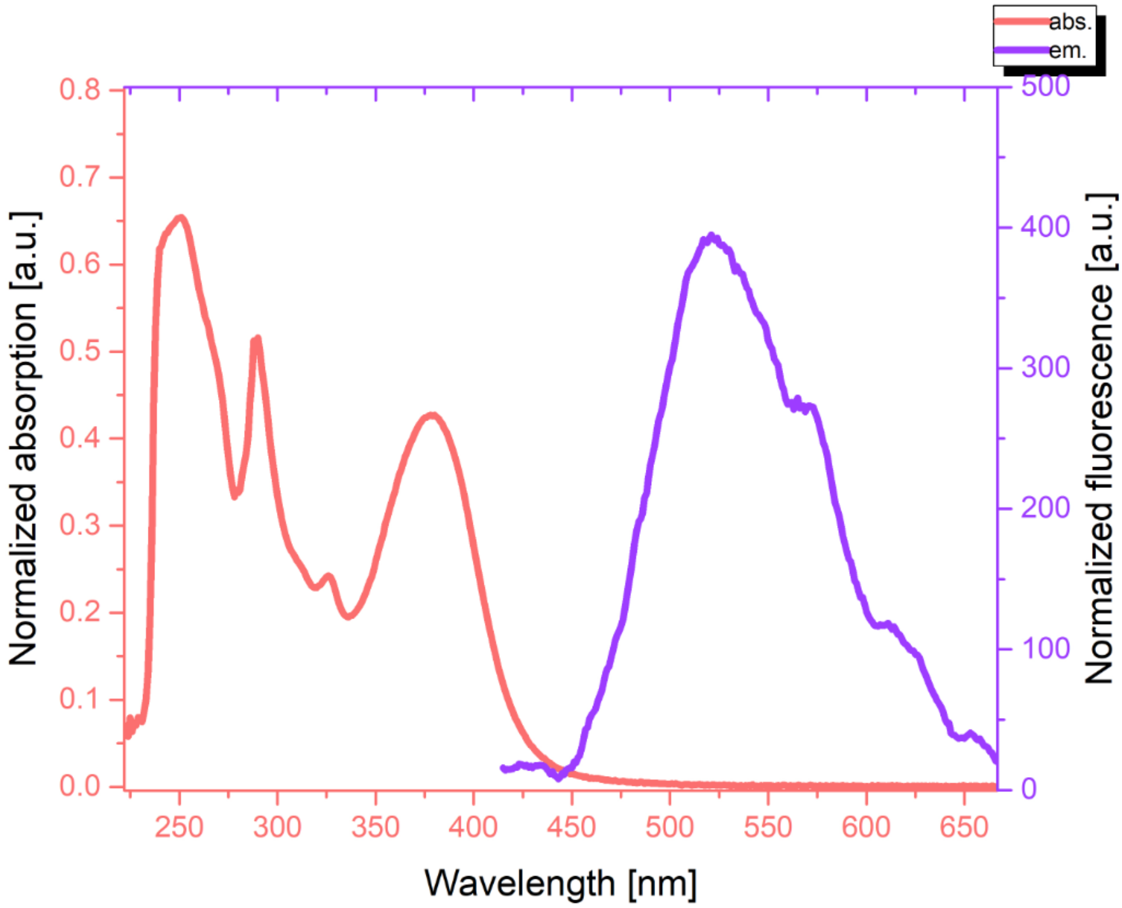


Figure S4. Normalized absorption and emission spectra for compound **5a** in **THF** (T = 293 °C, λ_{exc} = 365 nm).

4.5 Absorption and Emission of Compound 5a in Acetone

Table S5. Photophysical properties of compound **5a** recorded in **Acetone**

Compound	$\lambda_{max,abs}$ [nm][a]	$\lambda_{max,em}$ [nm][b]	Stokes shift [nm]
5a	377	571	194

[a]Recorded in Acetone, *T* = 293 K, *c* =6.5×10^{-5} M. [b]Recorded in Acetone, *T* = 293 K, *c*=6.5×10^{-6} M.

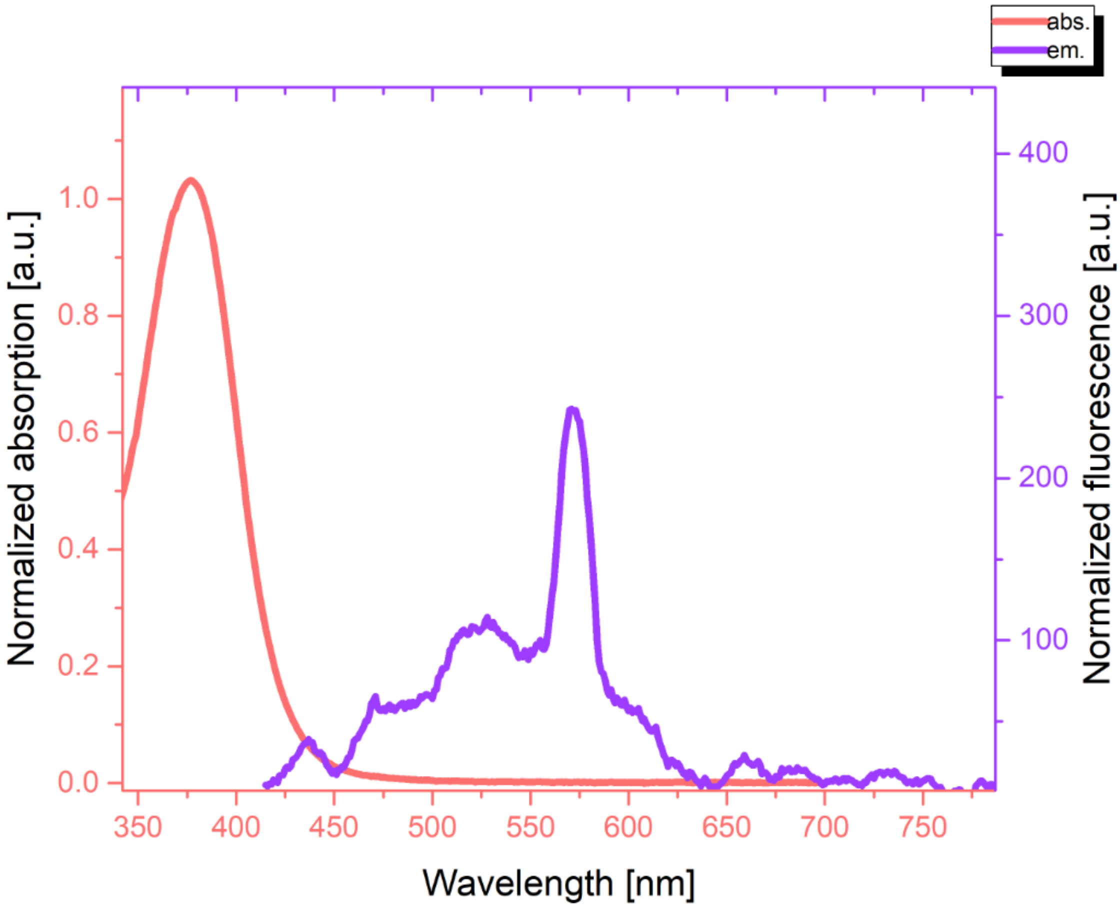


Figure S5. Normalized absorption and emission spectra for compound **5a** in **Acetone** (T = 293 °C, λ_{exc} = 365 nm).

4.6 Absorption and Emission of Compound 5a in Dioxane

Table S6. Photophysical properties of compound **5a** recorded in **Dioxane**

Compound	$\lambda_{max,abs}$ [nm][a]	$\lambda_{max,em}$ [nm][b]	Stokes shift [nm]
5a	375	520	145

[a]Recorded in Dioxane, T = 293 K, c =6.5×10^{-5} M. [b]Recorded in Dioxane, T = 293 K, c=6.5×10^{-6} M.

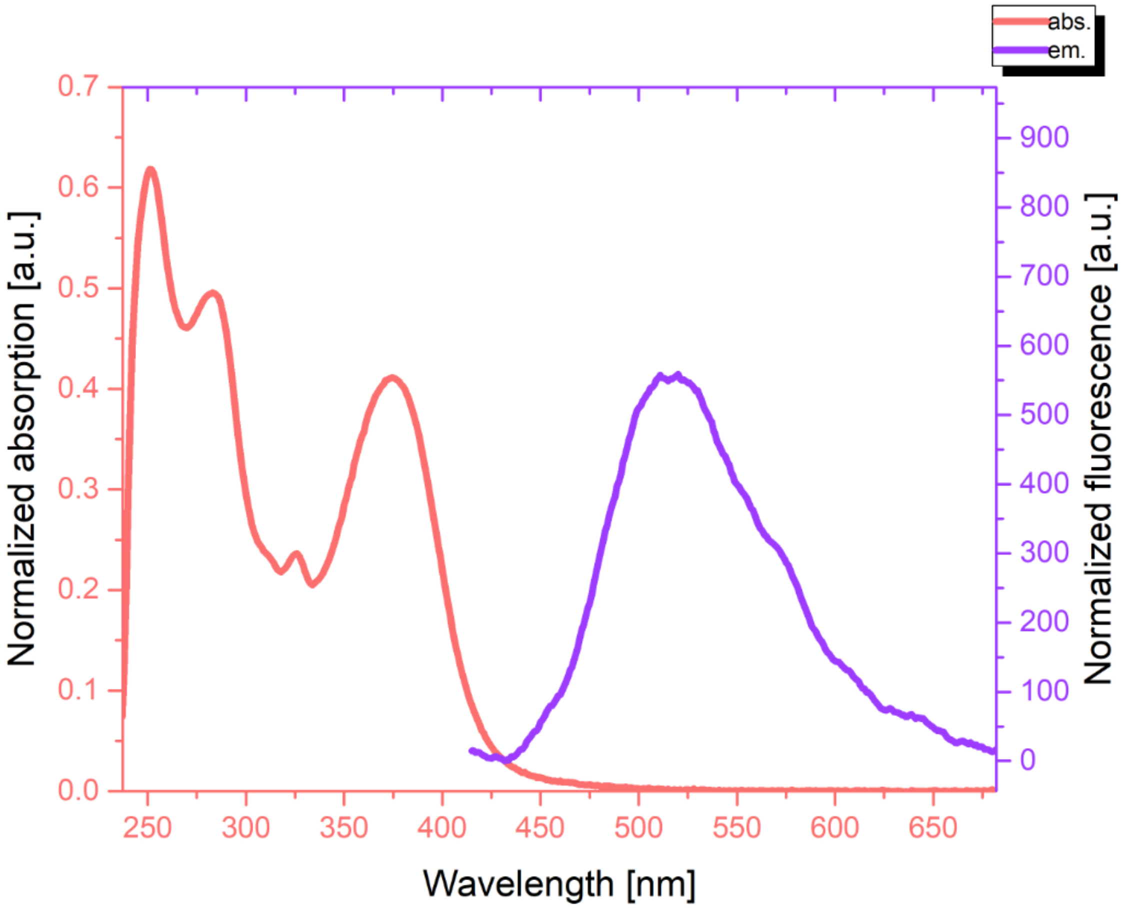


Figure S6. Normalized absorption and emission spectra for compound **5a** in **Dioxane** (T = 293 °C, λ_{exc} = 365 nm).

4.7 Absorption and Emission of Compound 5a in Ethyl acetate

Table S7. Photophysical properties of compound **5a** recorded in **Ethyl acetate**

Compound	$\lambda_{max,abs}$ [nm][a]	$\lambda_{max,em}$ [nm][b]	Stokes shift [nm]
5a	375	534	159

[a]Recorded in Ethyl acetate, T = 293 K, c =6.5×10^{-5} M. [b]Recorded in Ethyl acetate, T = 293 K, c=6.5×10^{-6} M.

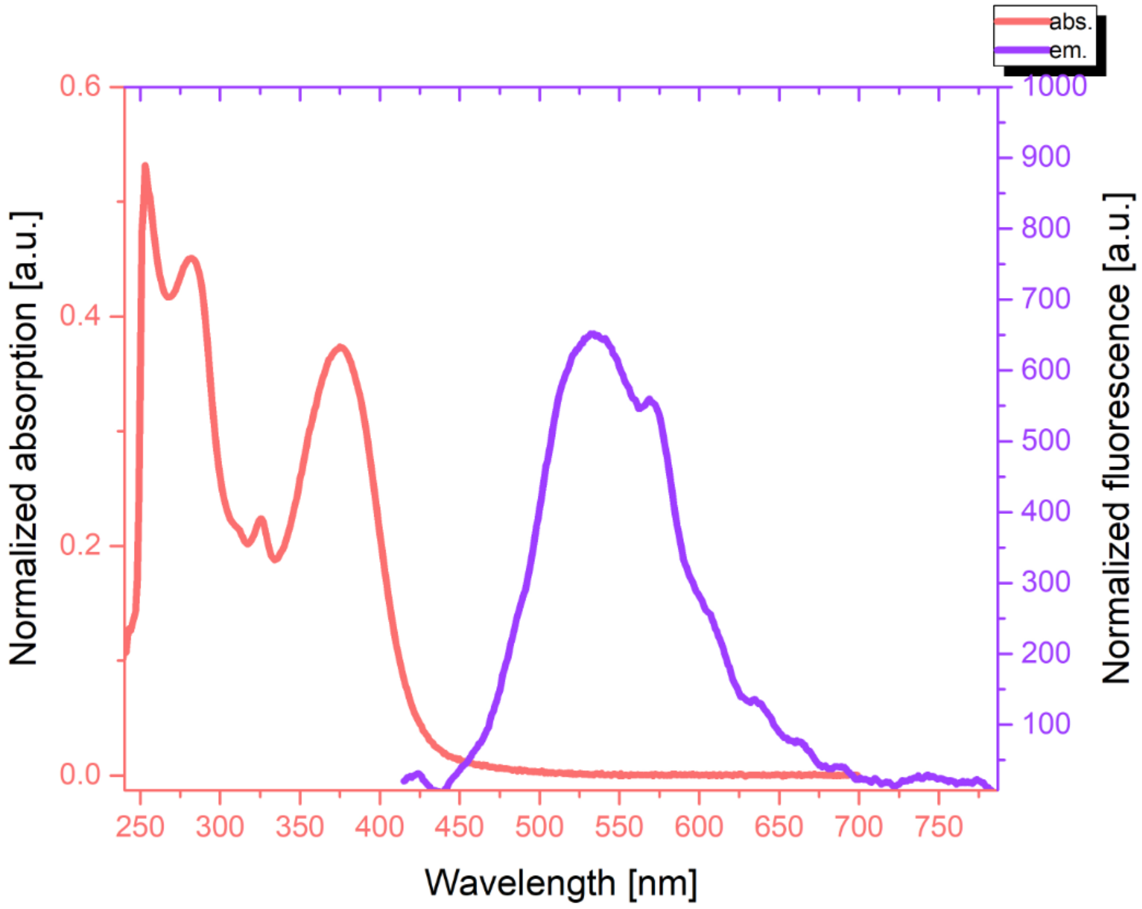


Figure S7. Normalized absorption and emission spectra for compound **5a** in **Ethyl acetate** (T = 293 °C, λ_{exc} = 365 nm).

4.8 Absorption and Emission of Compound 5a in DMF

Table S8. Photophysical properties of compound **5a** recorded in **DMF**

Compound	$\lambda_{max,abs}$ [nm][a]	$\lambda_{max,em}$ [nm][b]	Stokes shift [nm]
5a	384	571	187

[a]Recorded in DMF, *T* = 293 K, *c* =6.5×10^{-5} M. [b]Recorded in DMF, *T* = 293 K, *c*=6.5×10^{-6} M.

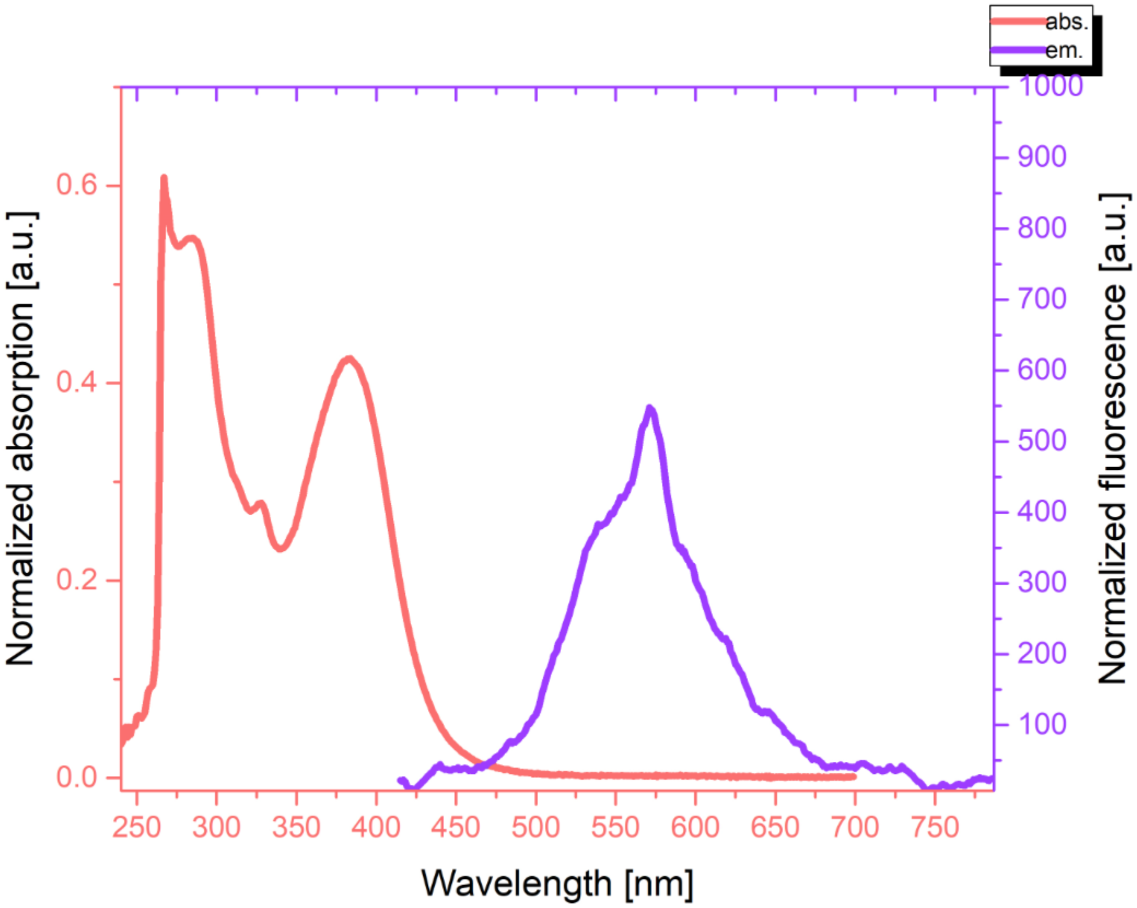


Figure S8. Normalized absorption and emission spectra for compound **5a** in **DMF** (T = 293 °C, λ_{exc} = 365 nm).

4.9 Absorption and Emission of Compound 5a in DMSO

Table S9. Photophysical properties of compound **5a** recorded in **DMSO**

Compound	$\lambda_{max,abs}$ [nm][a]	$\lambda_{max,em}$ [nm][b]	Stokes shift [nm]
5a	387	569	182

[a]Recorded in DMSO, *T* = 293 K, *c* =6.5×10^{-5} M. [b]Recorded in DMSO, *T* = 293 K, *c*=6.5×10^{-6} M.

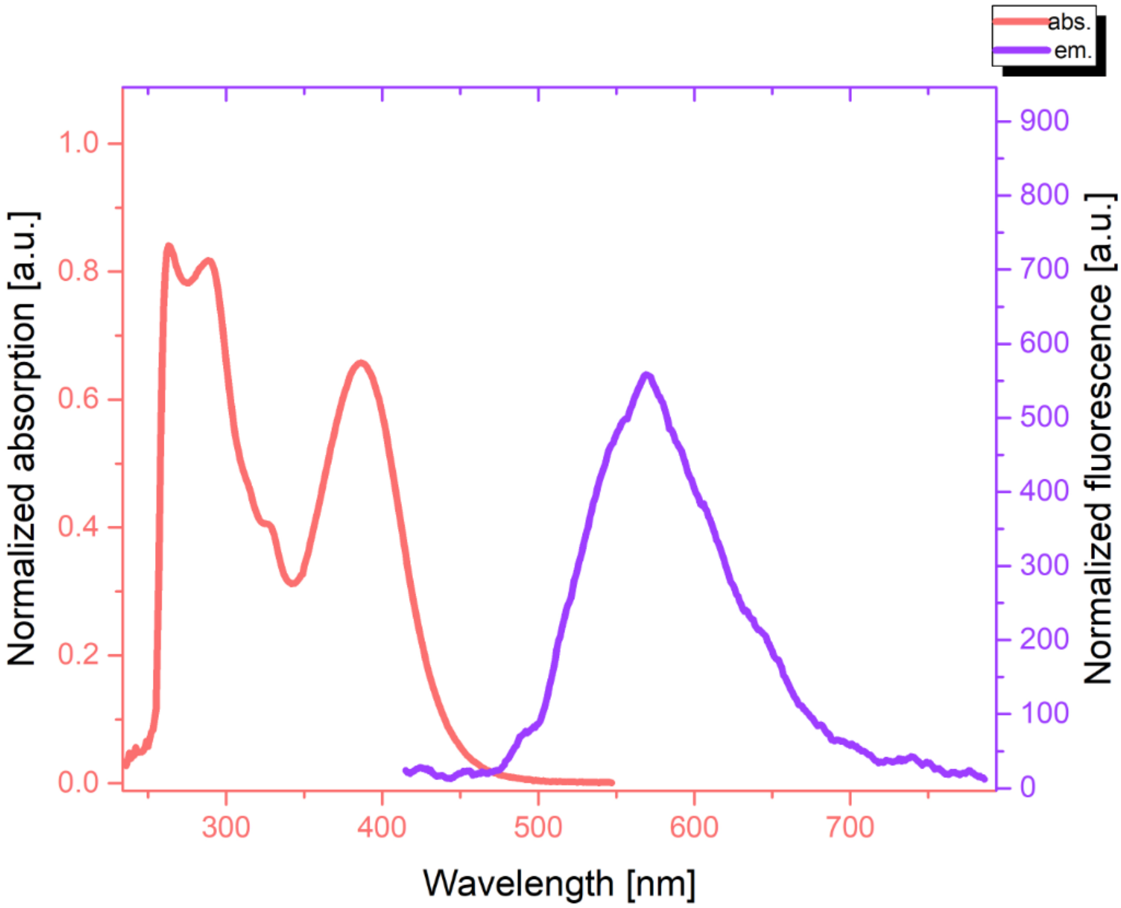


Figure S9. Normalized absorption and emission spectra for compound **5a** in **DMSO** (T = 293 °C, λ_{exc} = 365 nm).

4.10 Absorption and Emission of Compound 5a in CH_3CN

Table S10. Photophysical properties of compound **5a** recorded in **CH_3CN**

Compound	$\lambda_{max,abs}$ [nm][a]	$\lambda_{max,em}$ [nm][b]	Stokes shift [nm]
5a	371	573	202

[a]Recorded in CH_3CN, T = 293 K, c =6.5×10^{-5} M. [b]Recorded in CH_3CN, T = 293 K, c=6.5×10^{-6} M.

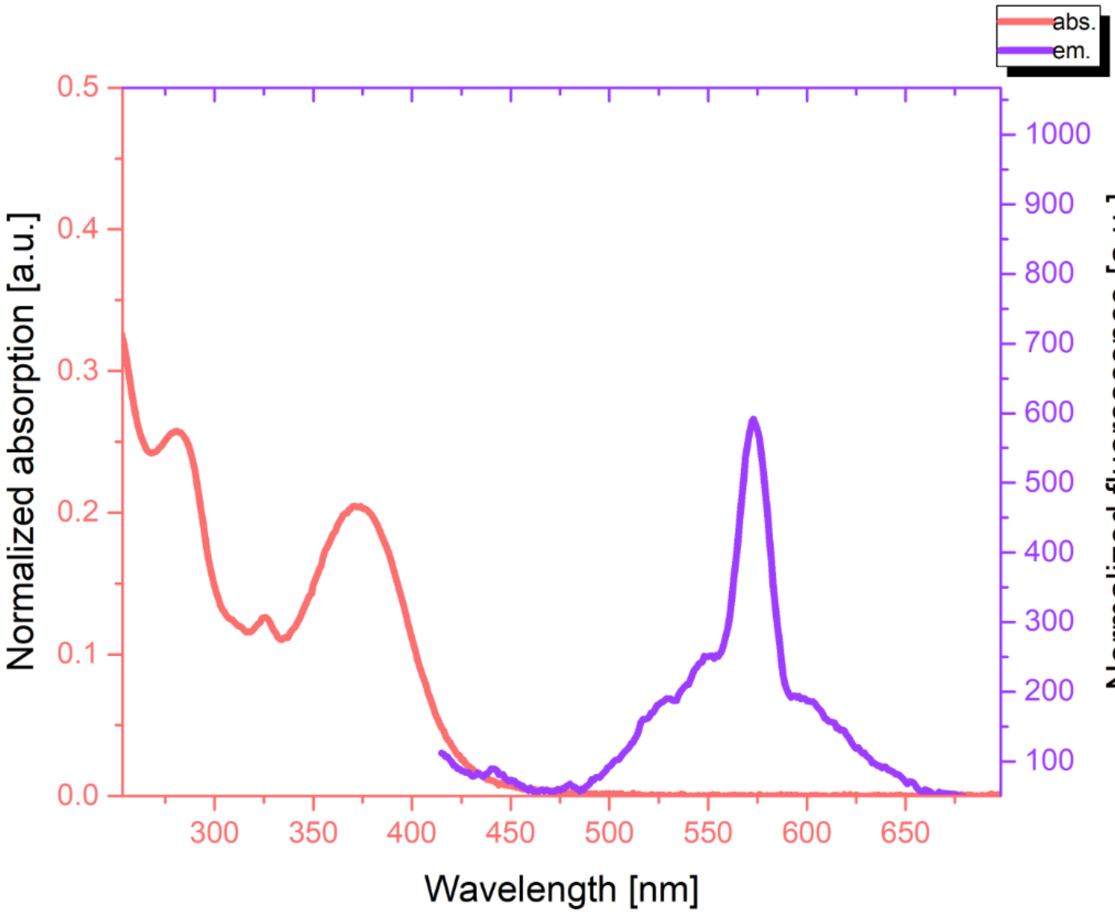


Figure S10. Normalized absorption and emission spectra for compound **5a** in **CH_3CN** (T = 293 °C, λ_{exc} = 365 nm).

4.11 Absorption and Emission of Compound 5a in EtOH

Table S11. Photophysical properties of compound **5a** recorded in **EtOH**

Compound	$\lambda_{max,abs}$ [nm][a]	$\lambda_{max,em}$ [nm][b]	Stokes shift [nm]
5a	383	573	190

[a]Recorded in EtOH, *T* = 293 K, *c* =6.5×10^{-5} M. [b]Recorded in EtOH, *T* = 293 K, *c*=6.5×10^{-6} M.

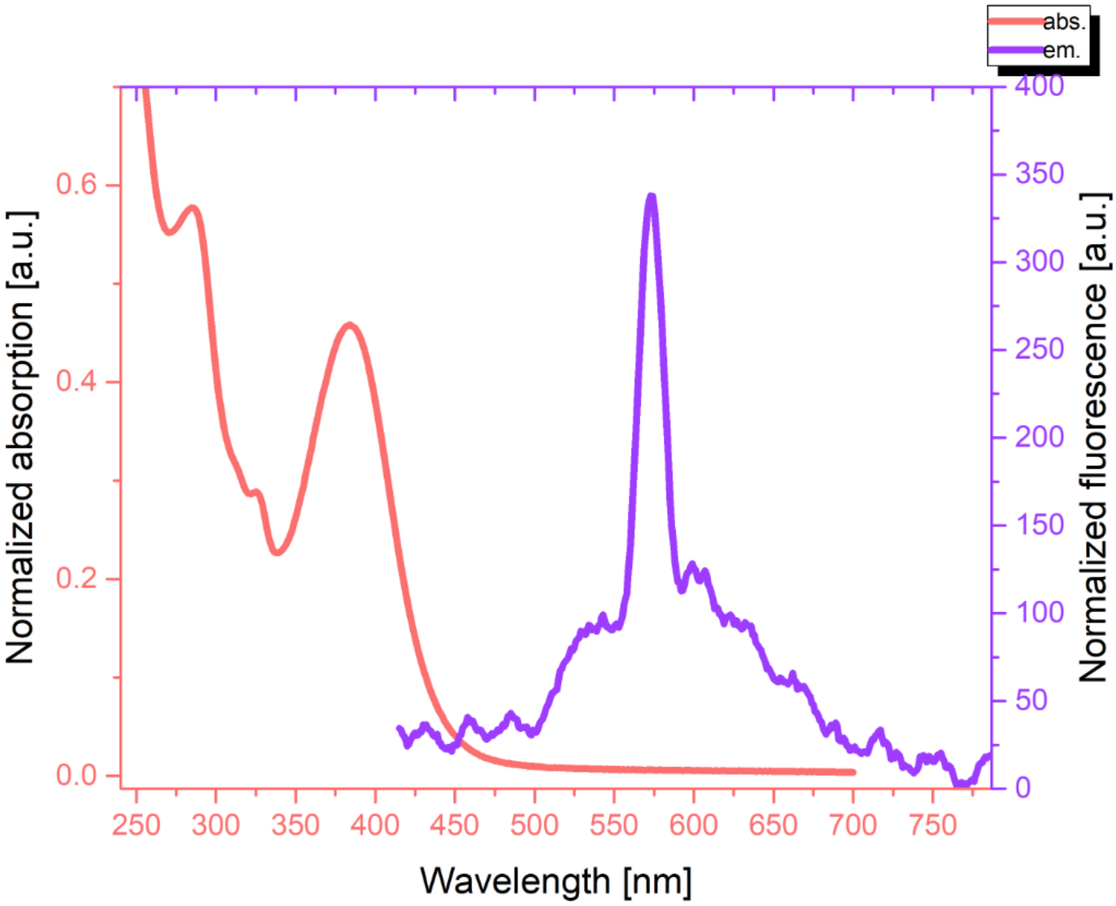


Figure S11. Normalized absorption and emission spectra for compound **5a** in **EtOH** (T = 293 °C, λ_{exc} = 365 nm).

4.12 Absorption and Emission of Compound 5a in MeOH

Table S12. Photophysical properties of compound **5a** recorded in **MeOH**

Compound	$\lambda_{max,abs}$ [nm][a]	$\lambda_{max,em}$ [nm][b]	Stokes shift [nm]
5a	381	573	192

[a]Recorded in MeOH, T = 293 K, c =6.5×10^{-5} M. [b]Recorded in MeOH, T = 293 K, c=6.5×10^{-6} M.

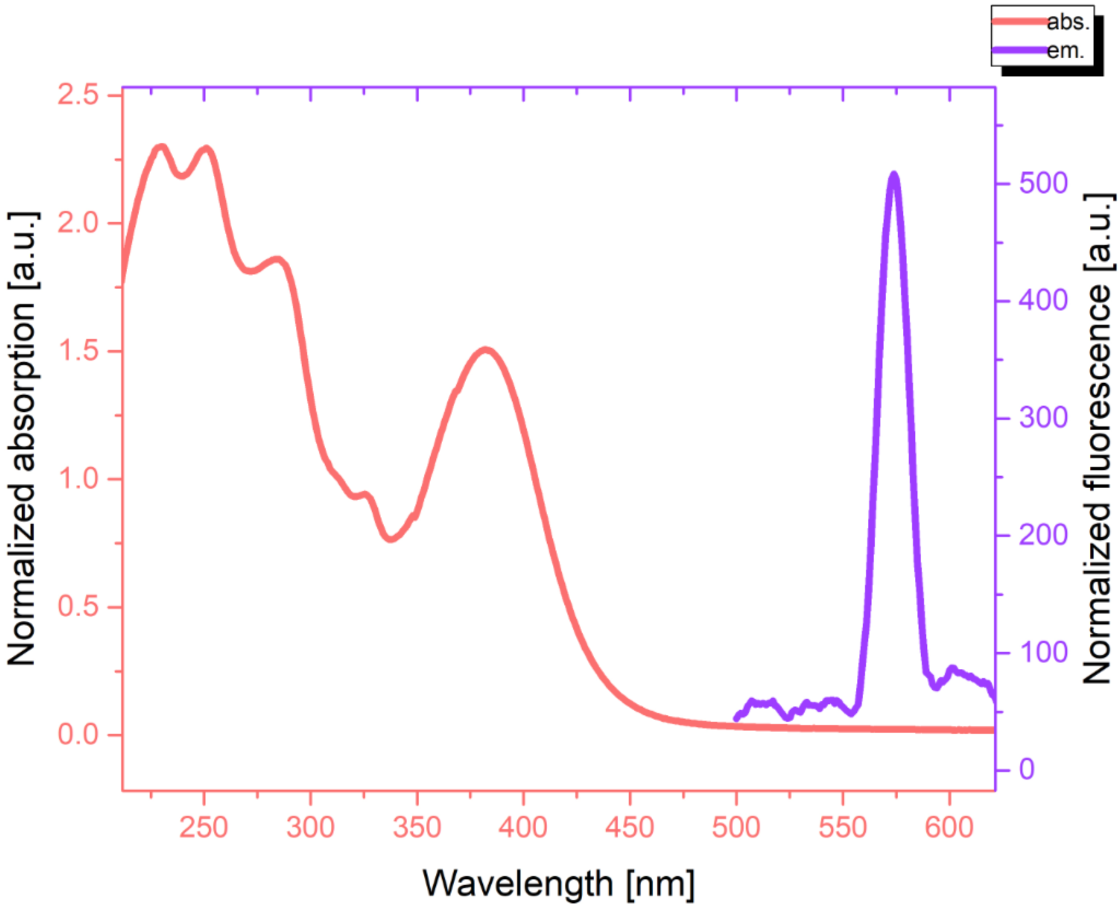


Figure S12. Normalized absorption and emission spectra for compound **5a** in **MeOH** (T = 293 °C, λ_{exc} = 365 nm).

4.13 Absorption and Emission of Compound 5a in CH_3COOH

Table S13. Photophysical properties of compound **5a** recorded in **CH_3COOH**

Compound	$\lambda_{max,abs}$ [nm][a]	$\lambda_{max,em}$ [nm][b]	Stokes shift [nm]
5a	336	573	237

[a]Recorded in CH_3COOH, T = 293 K, c =6.5×10^{-5} M. [b]Recorded in CH_3COOH, T = 293 K, c=6.5×10^{-6} M.

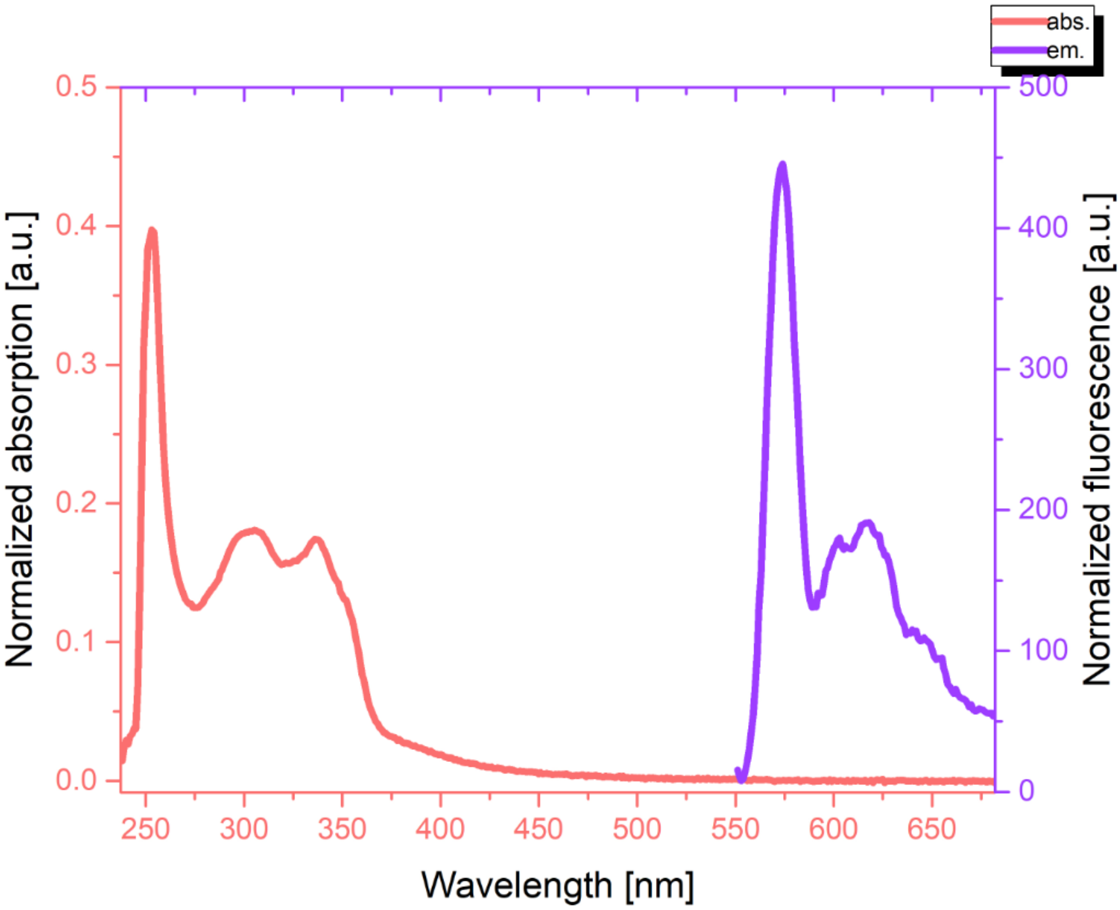


Figure S13. Normalized absorption and emission spectra for compound **5a** in **CH_3COOH** (T = 293 °C, λ_{exc} = 365 nm).

4.14 Absorption and Emission of Compound 5a in H_2O

Table S14. Photophysical properties of compound **5a** recorded in **H_2O**

Compound	$\lambda_{max,abs}$ [nm][a]	$\lambda_{max,em}$ [nm][b]	Stokes shift [nm]
5a	387	573	186

[a]Recorded in H_2O, T = 293 K, c =6.5×10^{-5} M. [b]Recorded in H_2O, T = 293 K, c=6.5×10^{-6} M.

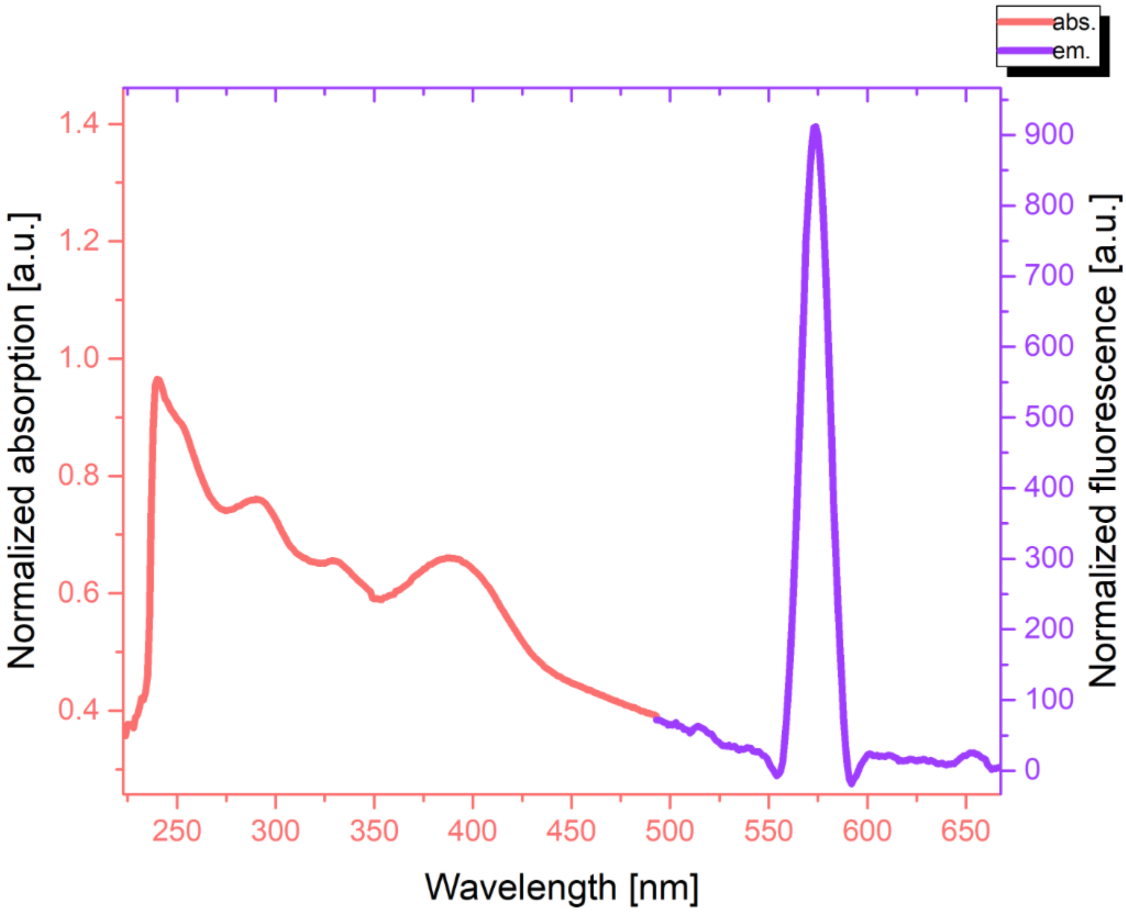
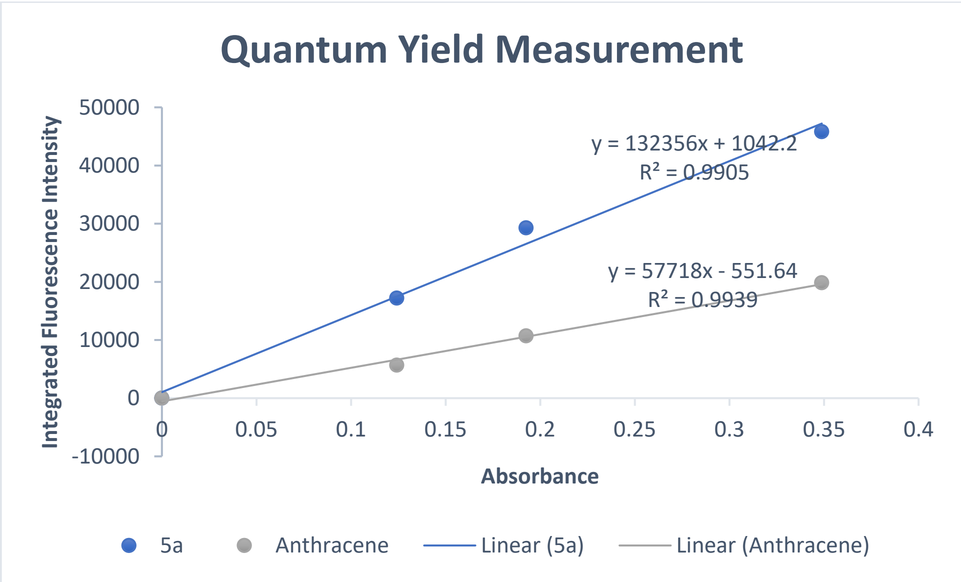


Figure S14. Normalized absorption and emission spectra for compound **5a** in **H_2O** (T = 293 °C, λ_{exc} = 365 nm).

4.15 Quantum Yield Data

The quantum yield for 5a in ethyl acetate was determined by using anthracene in ethyl acetate as a standard. Excitation occurred at 365 nm. The fluorescence of **5a** was integrated from 400 – 585 nm. The fluorescence of anthracene was integrated from 360 – 480 nm.[S3, S4]



5. References

[S1] J. Valencia, O. A. Sánchez-Velasco, J. Saavedra-Olavarría, P. Hermosilla-Ibáñez and E. G. Pérez, *Molecules* 2022, **27**, 8345.

[S2] (*a*) T. Nanjo, C. Tsukano and Y. Takemoto, *Org Lett* 2012, **14**, 4270; (*b*) L. Saeifard, K. Amiri, F. Rominger, T. J. J Müller and S. Balalaie, *J Org Chem* 2023, **88**, 12519.

[S3] T. J.Sisto, X.Tian and R. Jasti, *J Org Chem* 2012, **77**, 5857.

[S4] C. Würth, M. Grabolle, J. Pauli, M. Spieles and U. Resch-Genger, *Nat. Protoc.*, 2013, **8**, 1535.

6. X-Ray Crystallographic Analysis

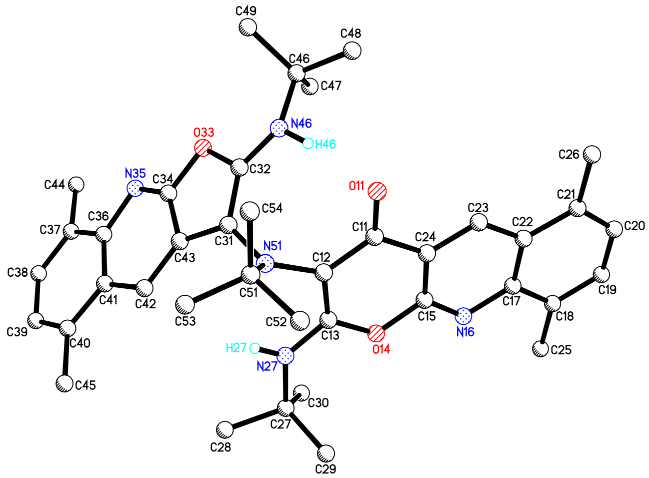


Table S15. Crystal data and structure refinement for sba175sq (**3d**).

Identification code	sba175sq	
Empirical formula	$C_{39}H_{47}N_5O_3$	
Formula weight	633.81	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Z	4	
Unit cell dimensions	a = 12.7784(7) Å	α = 90 deg.
	b = 25.7222(13) Å	β = 116.4726(16) deg.
	c = 12.9347(7) Å	γ = 90 deg.
Volume	3805.7(4) $Å^3$	
Density (calculated)	1.11 g/cm^3	
Absorption coefficient	0.07 mm^{-1}	
Crystal shape	brick	
Crystal size	0.115 x 0.086 x 0.078 mm^3	
Crystal colour	orange	
Theta range for data collection	1.6 to 25.1 deg.	
Index ranges	$-15\leq h\leq 15$, $-30\leq k\leq 30$, $-15\leq l\leq 15$	
Reflections collected	33716	
Independent reflections	6765 (R(int) = 0.0949)	
Observed reflections	3987 ($I > 2\sigma(I)$)	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.96 and 0.89	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	6765 / 408 / 446	
Goodness-of-fit on F^2	1.03	
Final R indices (I>2sigma(I))	R1 = 0.056, wR2 = 0.122	
Largest diff. peak and hole	0.17 and -0.27 $eÅ^{-3}$	

sba175sq: orange crystal (brick), dimensions 0.115 x 0.086 x 0.078 mm^3, crystal system monoclinic, space group $P2_1/n$, Z=4, a=12.7784(7) Å, b=25.7222(13) Å, c=12.9347(7) Å, alpha=90 deg, beta=116.4726(16) deg, gamma=90 deg, V=3805.7(4) $Å^3$, rho=1.106 g/cm^3, T=200(2) K, $Theta_{max}$= 25.082 deg, radiation MoKα, lambda=0.71073 Å, 0.5 deg omega-scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean redundancy of 4.90and a completeness of 99.8% to a resolution of 0.84 Å, 33716 reflections measured, 6765 unique (R(int)=0.0949), 3987 observed (I > 2σ(I)), intensities were corrected for Lorentz and polarization effects, an empirical scaling and absorption correction was applied using SADABS[1] based on the Laue symmetry of the reciprocal space, mu=0.07mm^{-1}, T_{min}=0.89, T_{max}=0.96, structure solved with SHELXT-2018/2 (Sheldrick 2015)[2] and refined against F^2 with a Full-matrix least-squares algorithm using the SHELXL-2019/2 (Sheldrick, 2019) software[3], 446 parameters refined, hydrogen atoms were treated using appropriate riding models, except H27 and H46 at the nitrogen atoms, which were refined isotropically, goodness of fit 1.03 for observed reflections, final residual values R1(F)=0.056, wR(F^2)=0.122 for observed reflections, residual electron density -0.27 to 0.17 eÅ^{-3}. CCDC 2401254 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Lit. 1: (SADABS-2016/2 - Bruker AXS area detector scaling and absorption correction)
Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10.

Lit. 2: (SHELXT - Integrated space-group and crystal structure determination)
Sheldrick G. M., Acta Cryst. A71 (2015) 3-8.

Lit. 3: (program SHELXL-2018/3 (Sheldrick, 2018) for structure refinement)
Sheldrick G. M., Acta Cryst. (2015). C71, 3-8

Lit. APEX, APEX2, SMART, SAINT, SAINT-Plus:
Bruker (2007). "Program name(s)". Bruker AXS Inc., Madison, Wisconsin, USA.

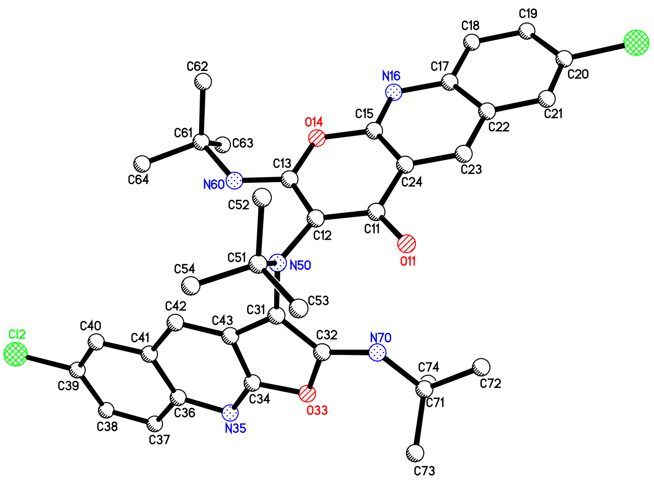


Table S16. Crystal data and structure refinement for sba172sq **(3j)**.

Identification code	sba172sq	
Empirical formula	$C_{35}H_{37}Cl_2N_5O_3$	
Formula weight	646.59	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P $\bar{1}$	
Z	2	
Unit cell dimensions	a = 10.6620(5) Å	α = 81.0768(10) deg.
	b = 10.8755(5) Å	β = 84.1741(10) deg.
	c = 19.5715(10) Å	γ = 64.0858(9) deg.
Volume	2015.06(17) Å^3	

Density (calculated)	1.07 g/cm^3
Absorption coefficient	0.20 mm^{-1}
Crystal shape	brick
Crystal size	0.110 x 0.087 x 0.052 mm^3
Crystal colour	orange
Theta range for data collection	2.1 to 26.8 deg.
Index ranges	$-13\leq h\leq 13$, $-13\leq k\leq 13$, $-24\leq l\leq 24$
Reflections collected	36449
Independent reflections	8617 (R(int) = 0.0365)
Observed reflections	5964 ($I > 2\sigma(I)$)
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.96 and 0.93
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8617 / 0 / 415
Goodness-of-fit on F^2	1.04
Final R indices (I>2sigma(I))	R1 = 0.053, wR2 = 0.137
Largest diff. peak and hole	0.59 and -0.39 eÅ^{-3}

sba172sq: orange crystal (brick), dimensions 0.110 x 0.087 x 0.052 mm^3, crystal system triclinic, space group P $\bar{1}$, Z=2, a=10.6620(5) Å, b=10.8755(5) Å, c=19.5715(10) Å, alpha=81.0768(10) deg, beta=84.1741(10) deg, gamma=64.0858(9) deg, V=2015.06(17) Å^3, rho=1.066 g/cm^3, T=200(2) K, Theta$_{max}$= 26.811 deg, radiation MoKα, lambda=0.71073 Å, 0.5 deg omega-scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean redundancy of 4.22and a completeness of 99.8% to a resolution of 0.79 Å, 36449 reflections measured, 8617 unique (R(int)=0.0365), 5964 observed ($I > 2\sigma(I)$), intensities were corrected for Lorentz and polarization effects, an empirical scaling and absorption correction was applied using SADABS[1] based on the Laue symmetry of the reciprocal space, mu=0.20mm^{-1}, T$_{min}$=0.93, T$_{max}$=0.96, structure solved with SHELXT-2018/2 (Sheldrick 2015)[2] and refined against F^2 with a Full-matrix least-squares algorithm using the SHELXL-2018/3 (Sheldrick, 2018) software[3], 415 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.04 for observed reflections, final residual values R1(F)=0.053, wR(F^2)=0.137 for observed reflections, residual electron density -0.39 to 0.59 eÅ^{-3}. CCDC 2401253 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Lit. 1: (SADABS-2016/2 - Bruker AXS area detector scaling and absorption correction)
Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10.

Lit. 2: (SHELXT - Integrated space-group and crystal structure determination)
Sheldrick G. M., Acta Cryst. A71 (2015) 3-8.

Lit. 3: (program SHELXL-2018/3 (Sheldrick, 2018) for structure refinement)
Sheldrick G. M., Acta Cryst. (2015). C71, 3-8

Lit. APEX, APEX2, SMART, SAINT, SAINT-Plus:
Bruker (2007). "Program name(s)". Bruker AXS Inc., Madison, Wisconsin, USA.

7. ^{1}H-NMR, ^{13}C-NMR, and HRMS-ESI of unknown compounds

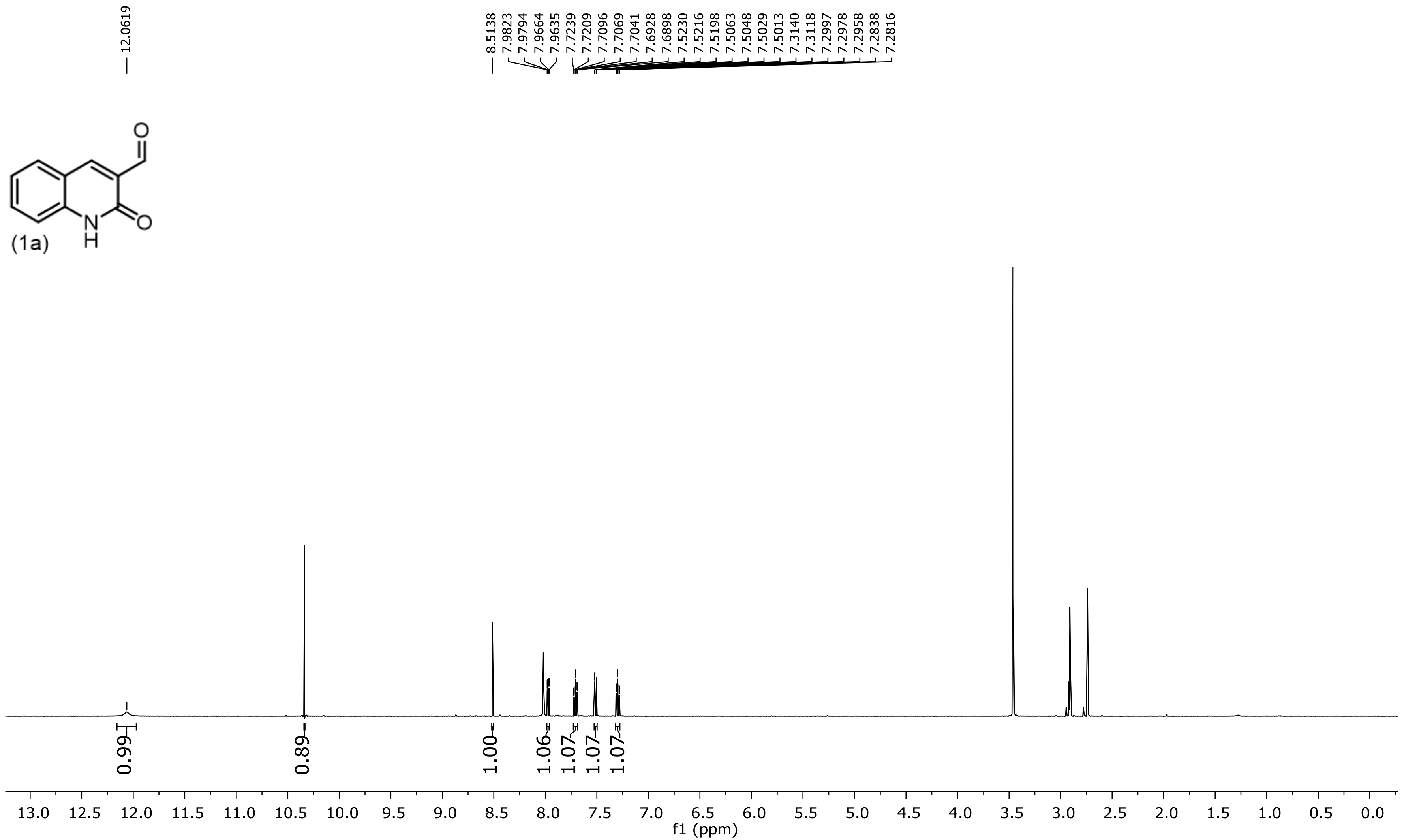


Figure S15. ^{1}H NMR 1a.

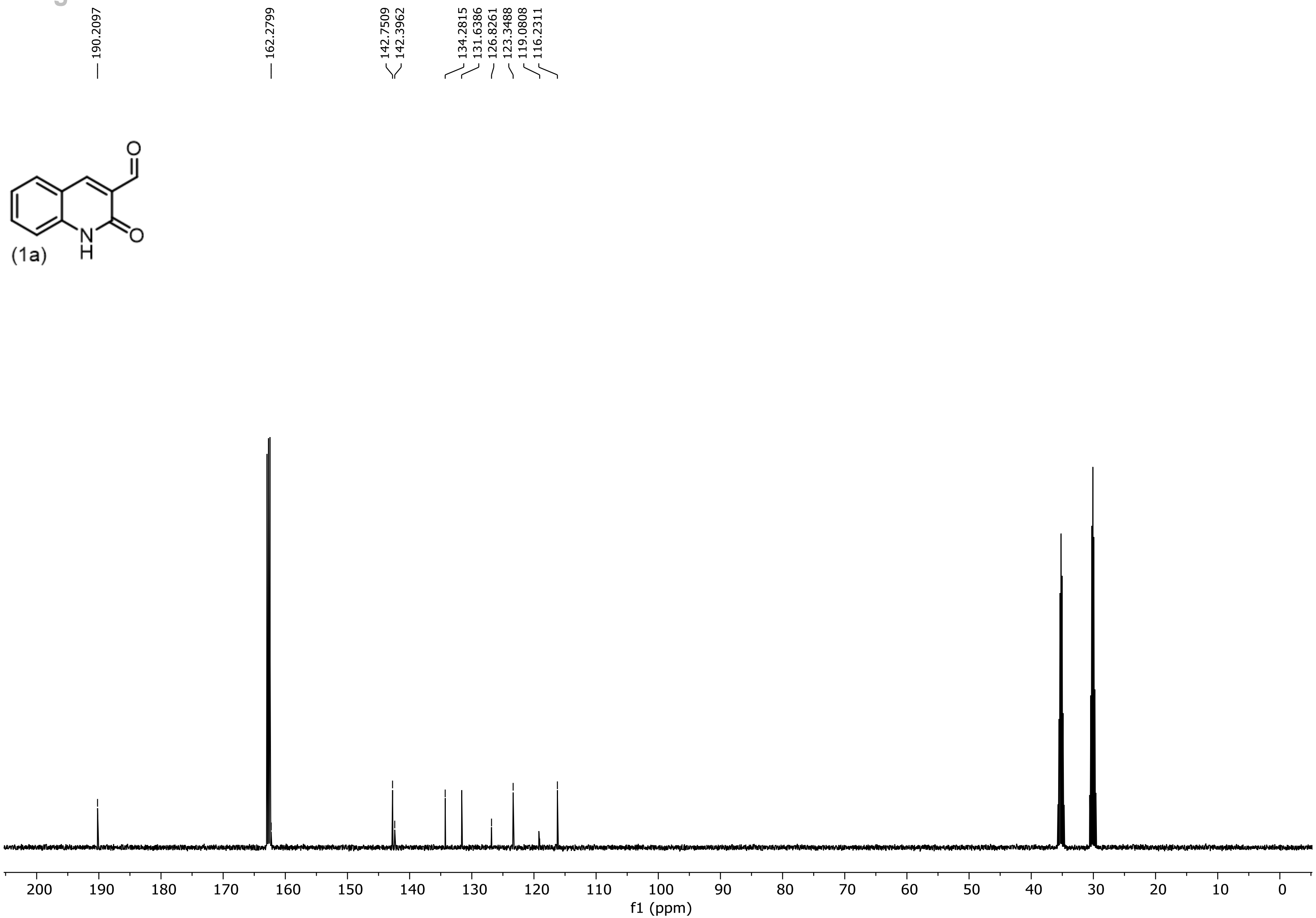
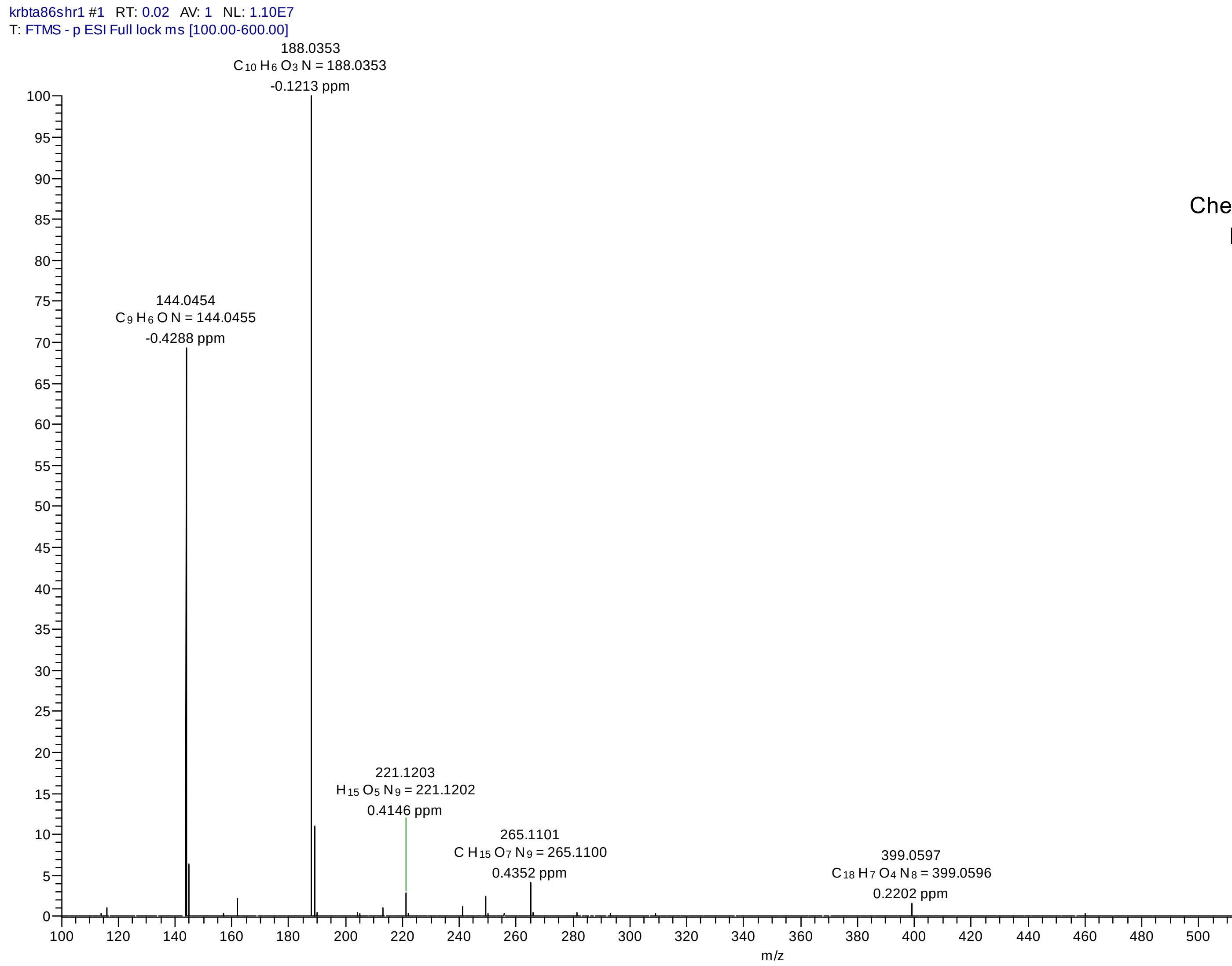
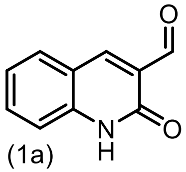


Figure S16. ^{13}C NMR 1a.

D:\data_2020\krbta86shr1 9/21/2020 11:14:40 AM





(1a)

Chemical Formula: $C_{10}H_7NO_2$
Exact Mass: 173.0477

Figure S17. HRMS-ESI 1a.

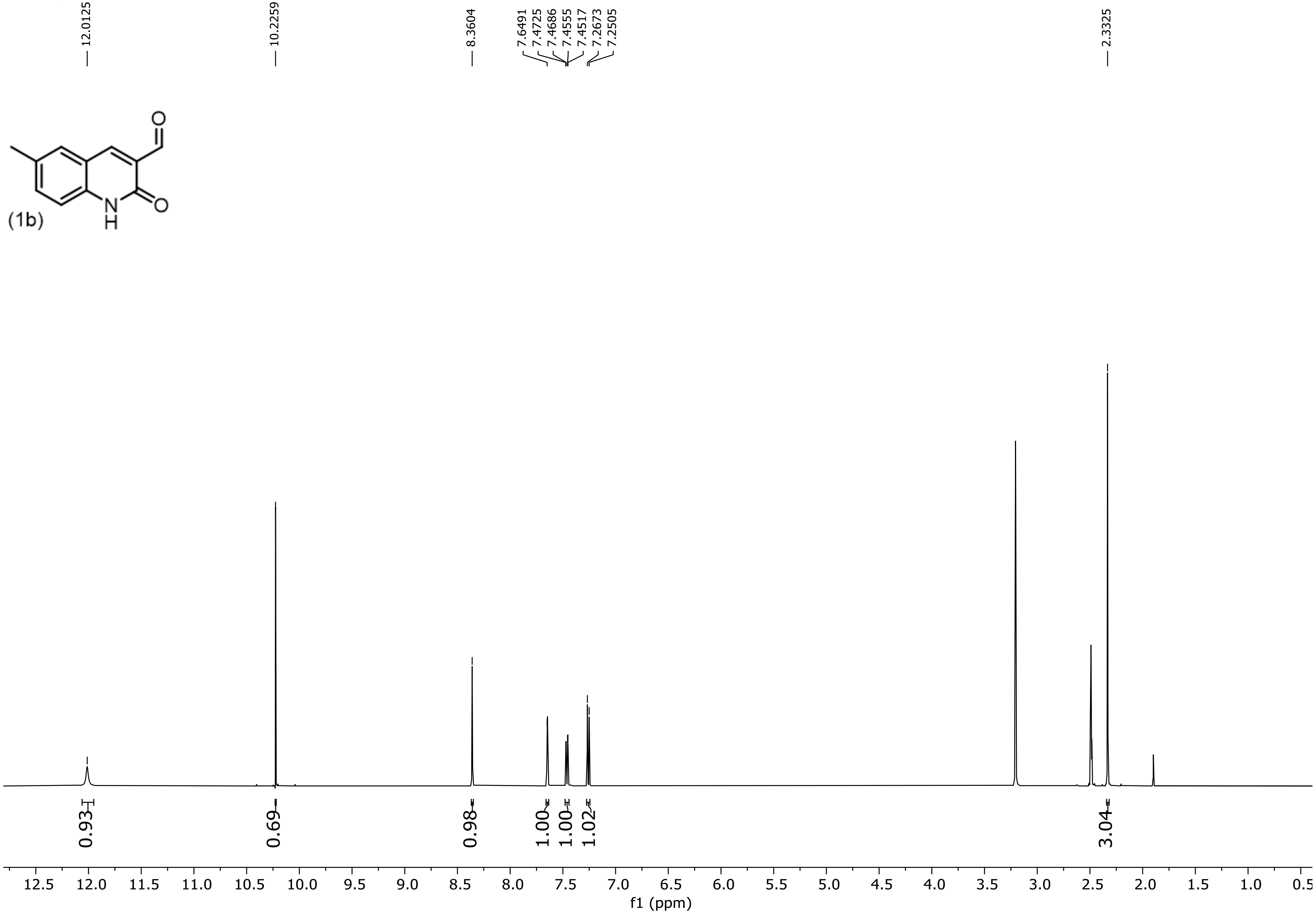
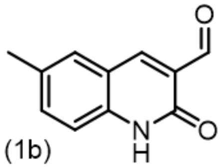


Figure S18. ^{1}H NMR 1b.



(1b)

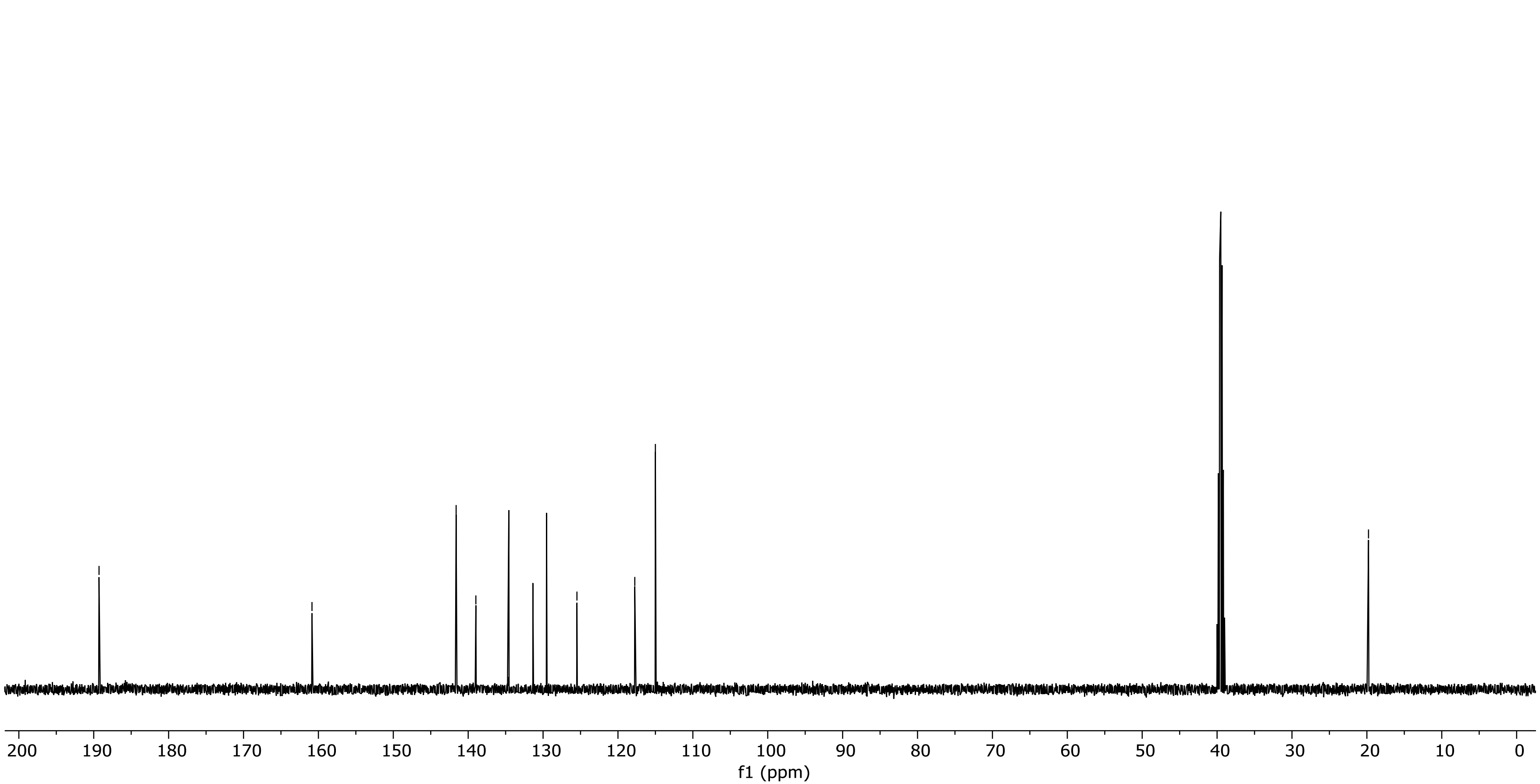


Figure S19. ^{13}C NMR 1b.

D:\data_2020\mobta04shr1 9/21/2020 11:52:06 AM

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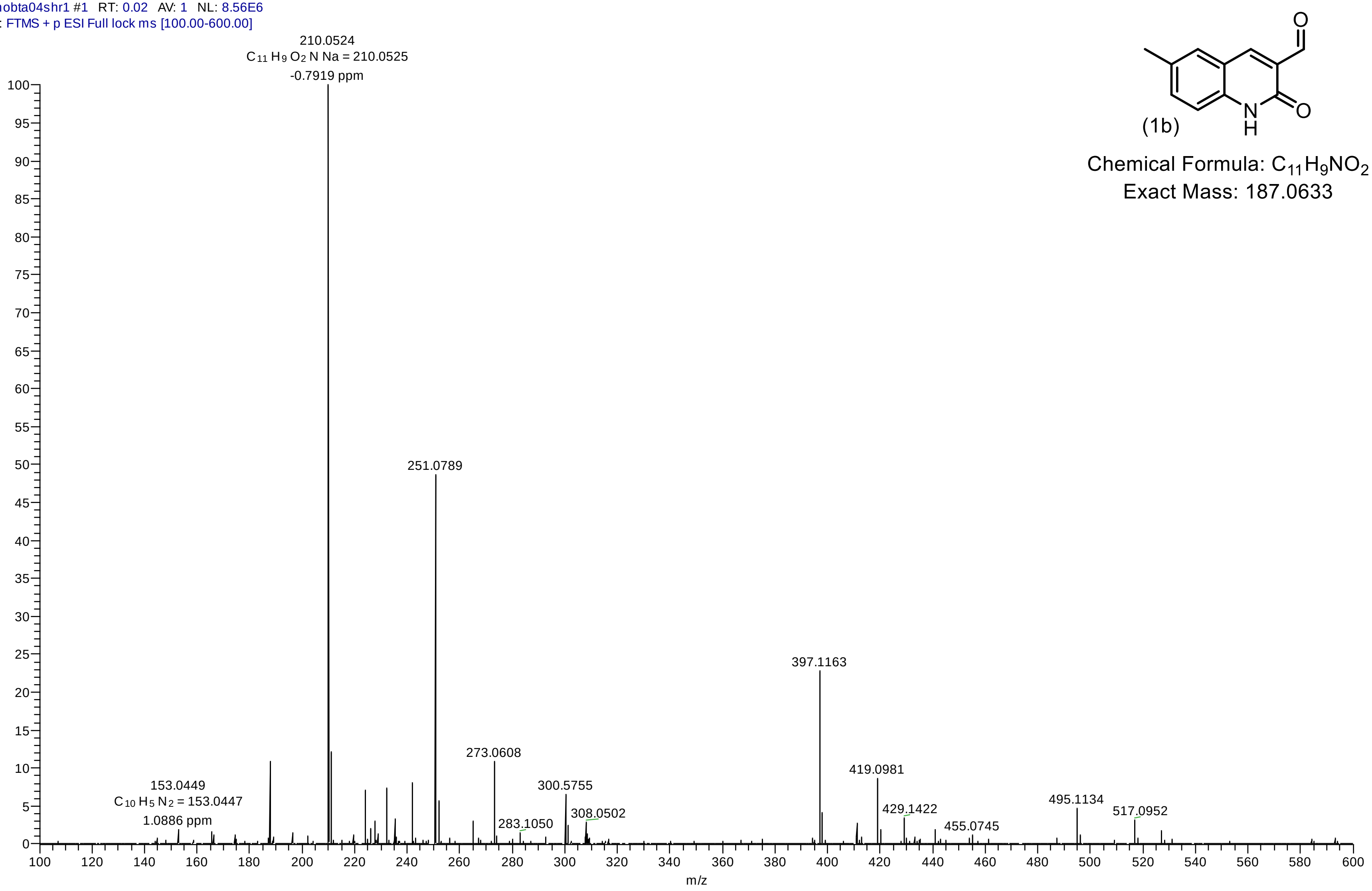


(1b)

Chemical Formula: $C_{11}H_9NO_2$
Exact Mass: 187.0633

Figure S20. HRMS-ESI 1b.

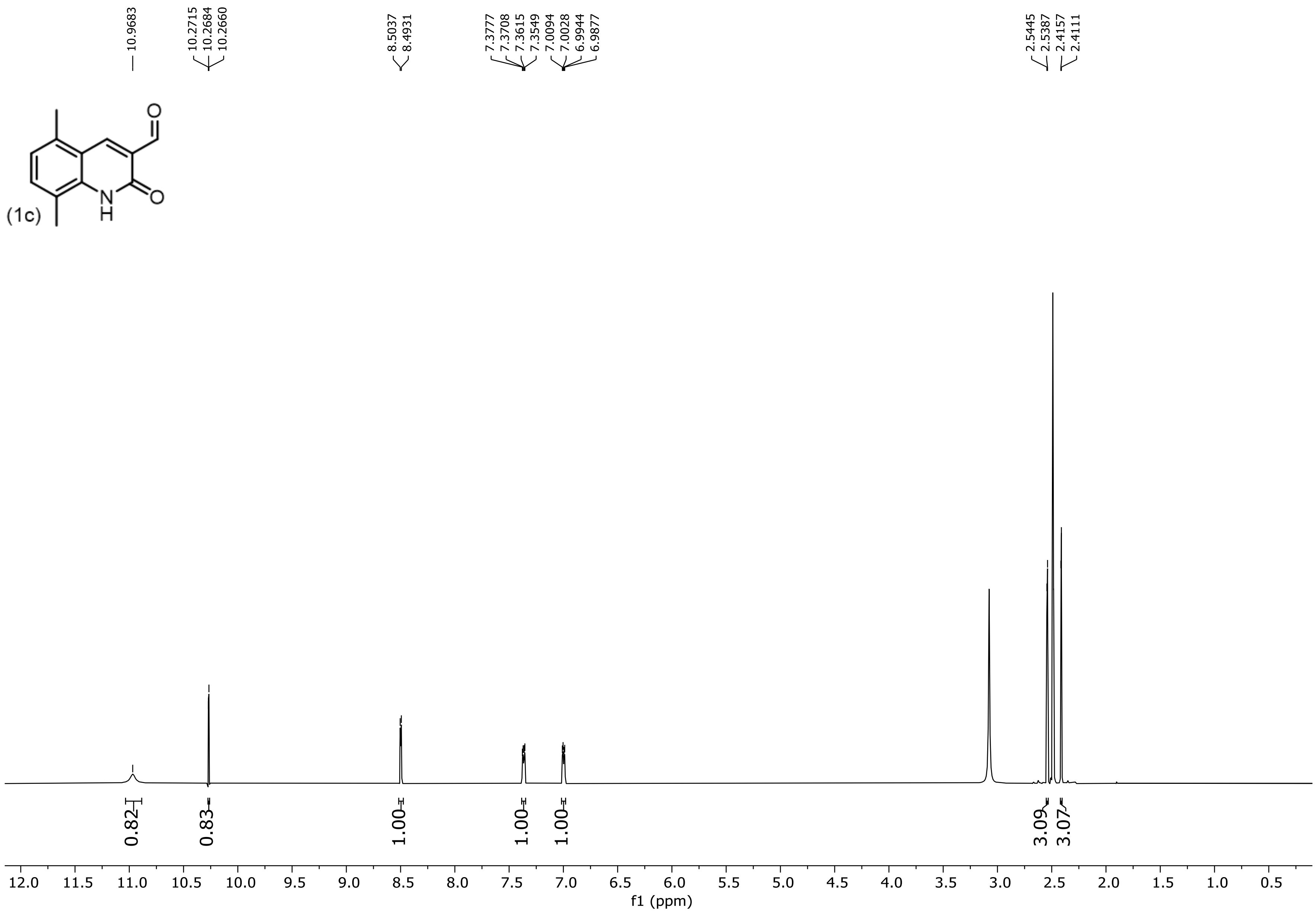


Figure S21. ^{1}H NMR 1c.

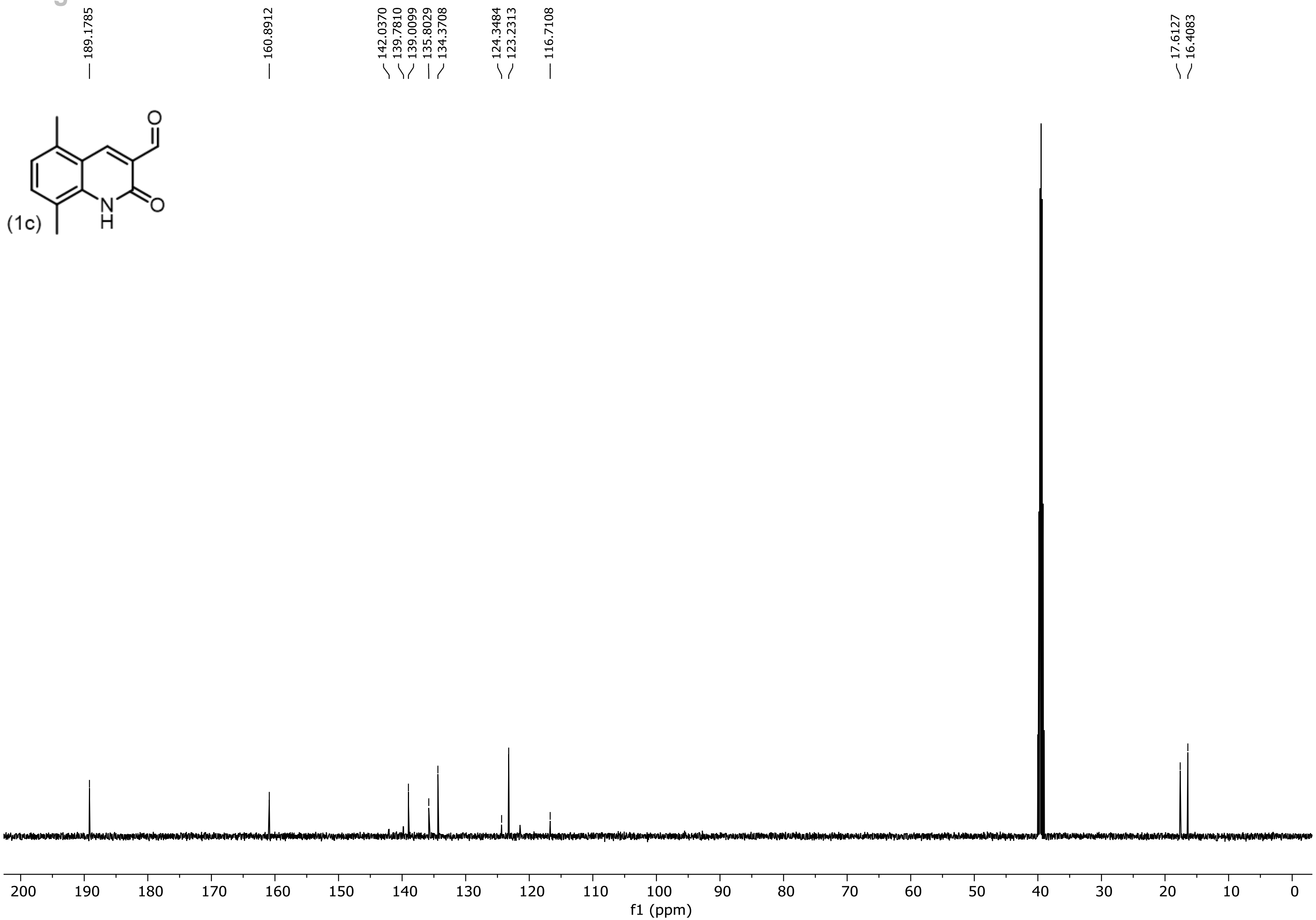
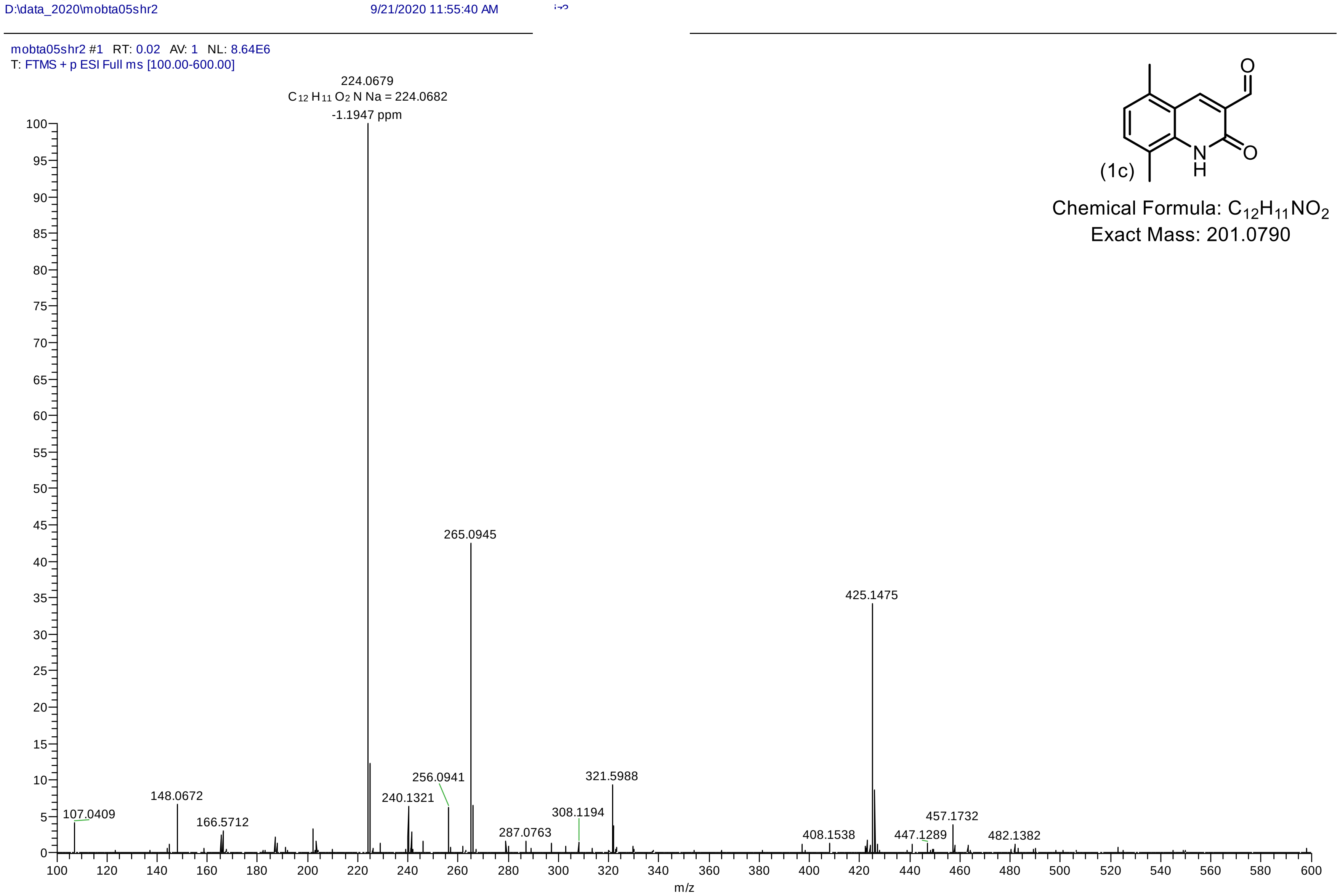


Figure S22. ^{13}**C NMR 1c.**



(1c)

Chemical Formula: $C_{12}H_{11}NO_2$

Exact Mass: 201.0790

Figure S23. HRMS-ESI 1c.

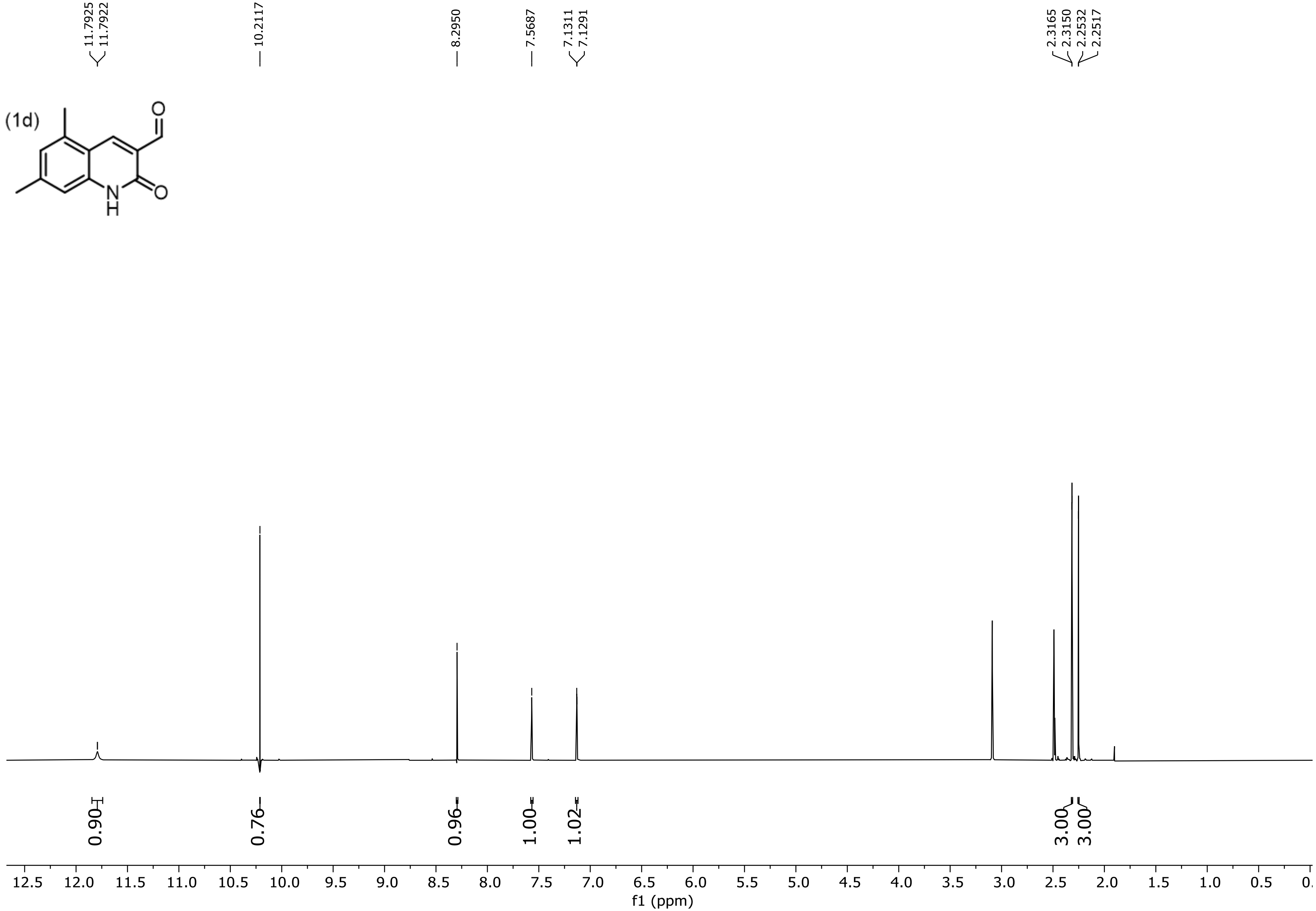


Figure S24. ^{1}H NMR 1d.

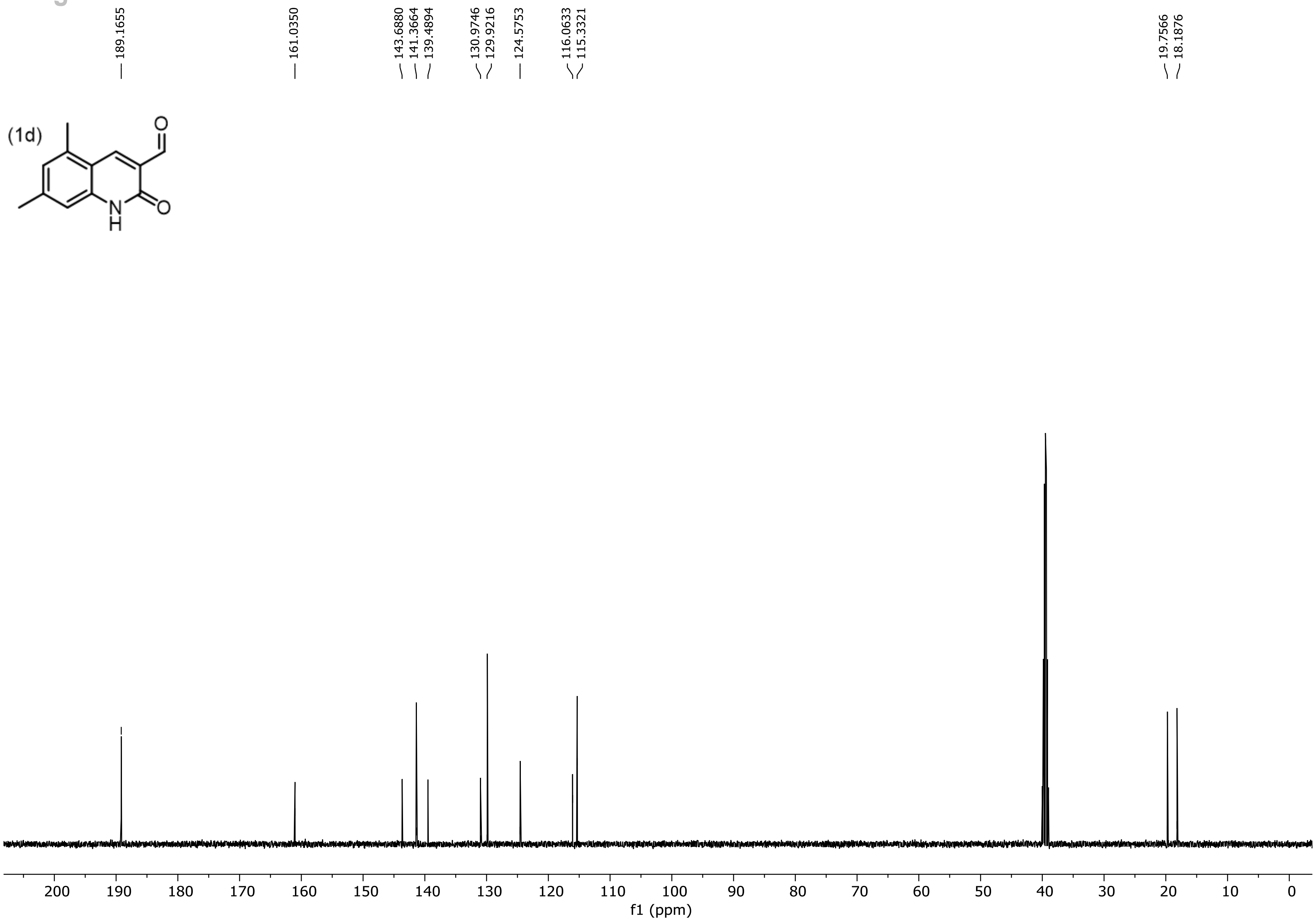


Figure S25. ^{13}C NMR 1d.

D:\data_2020\jnbta24shr2 9/21/2020 11:27:26 AM

jnbta24shr2 #1 RT: 0.02 AV: 1 NL: 7.80E6
T: FTMS + p ESI Full lock ms [100.00-600.00]

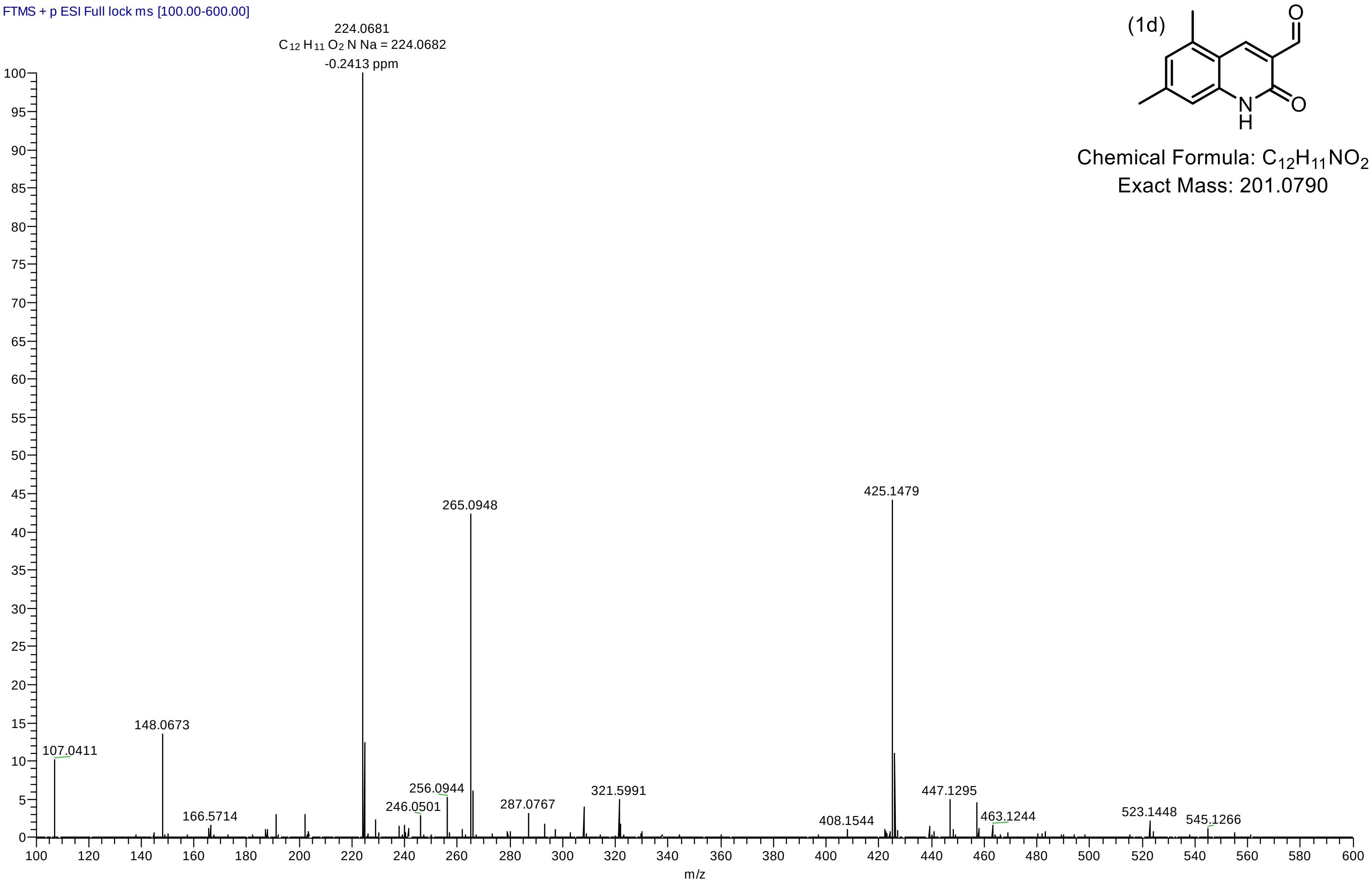
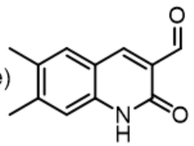


Figure S26. HRMS-ESI 1d.

(1e)



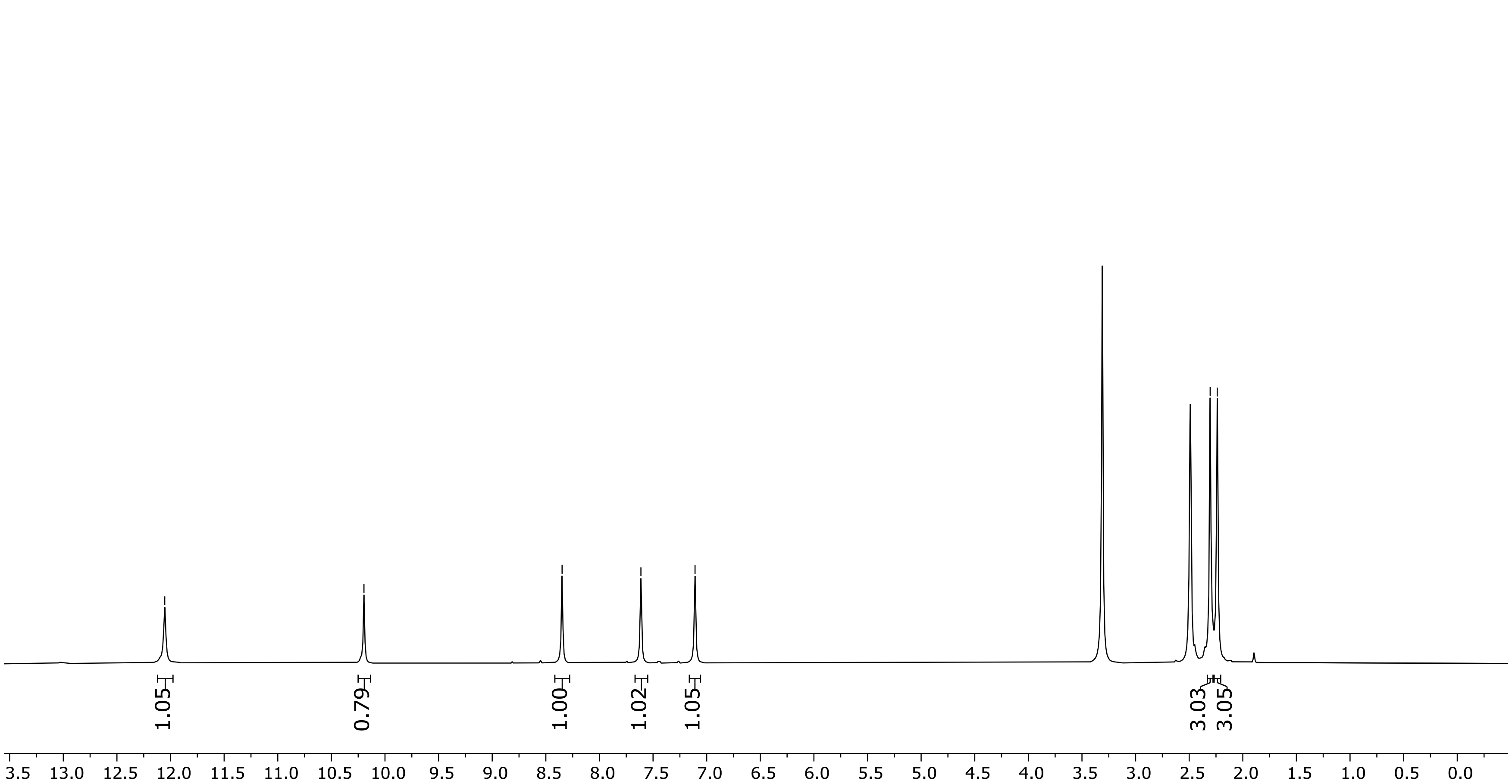


Figure S27. ^{1}H NMR 1e.

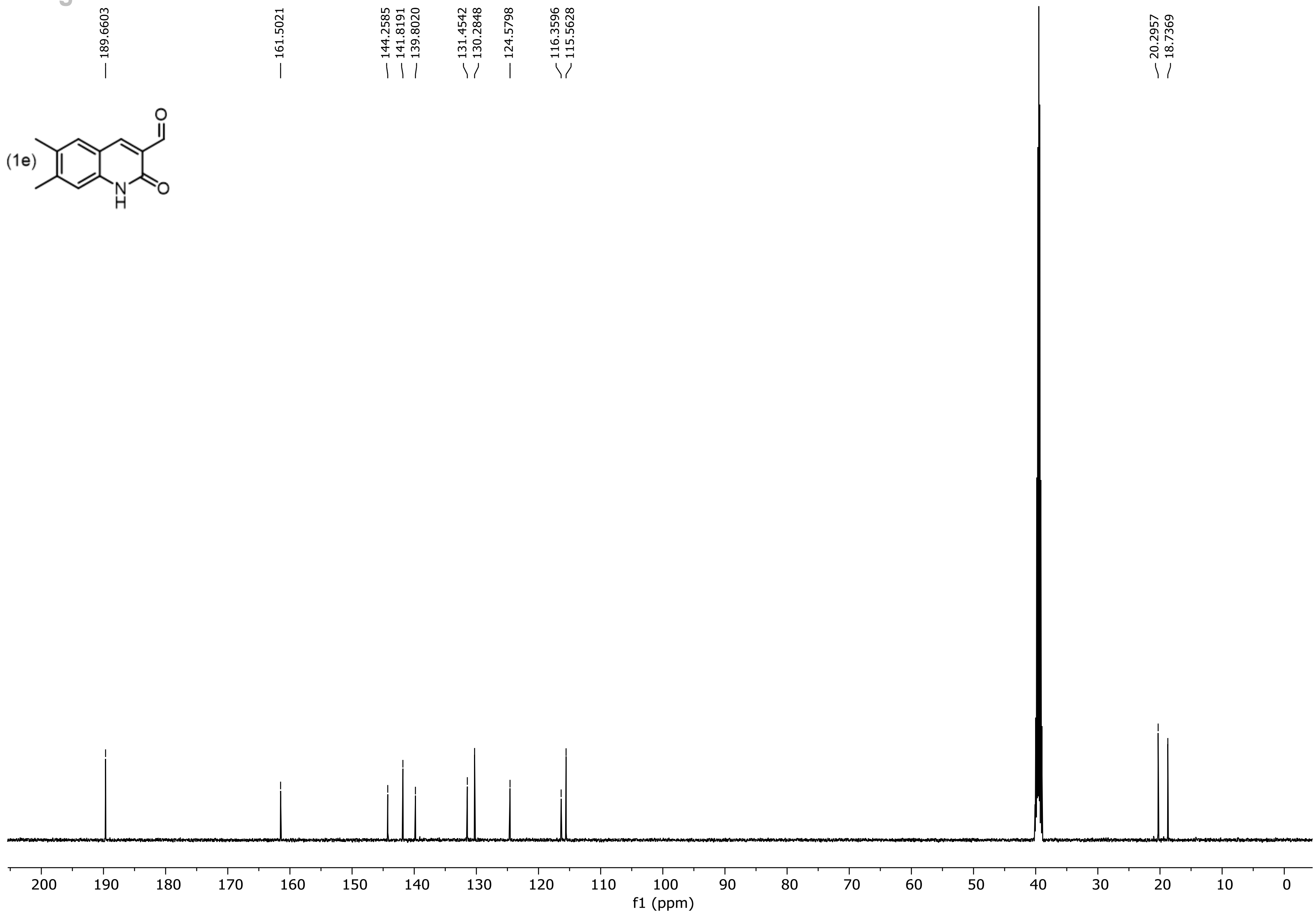


Figure S28. ^{13}C NMR 1e.

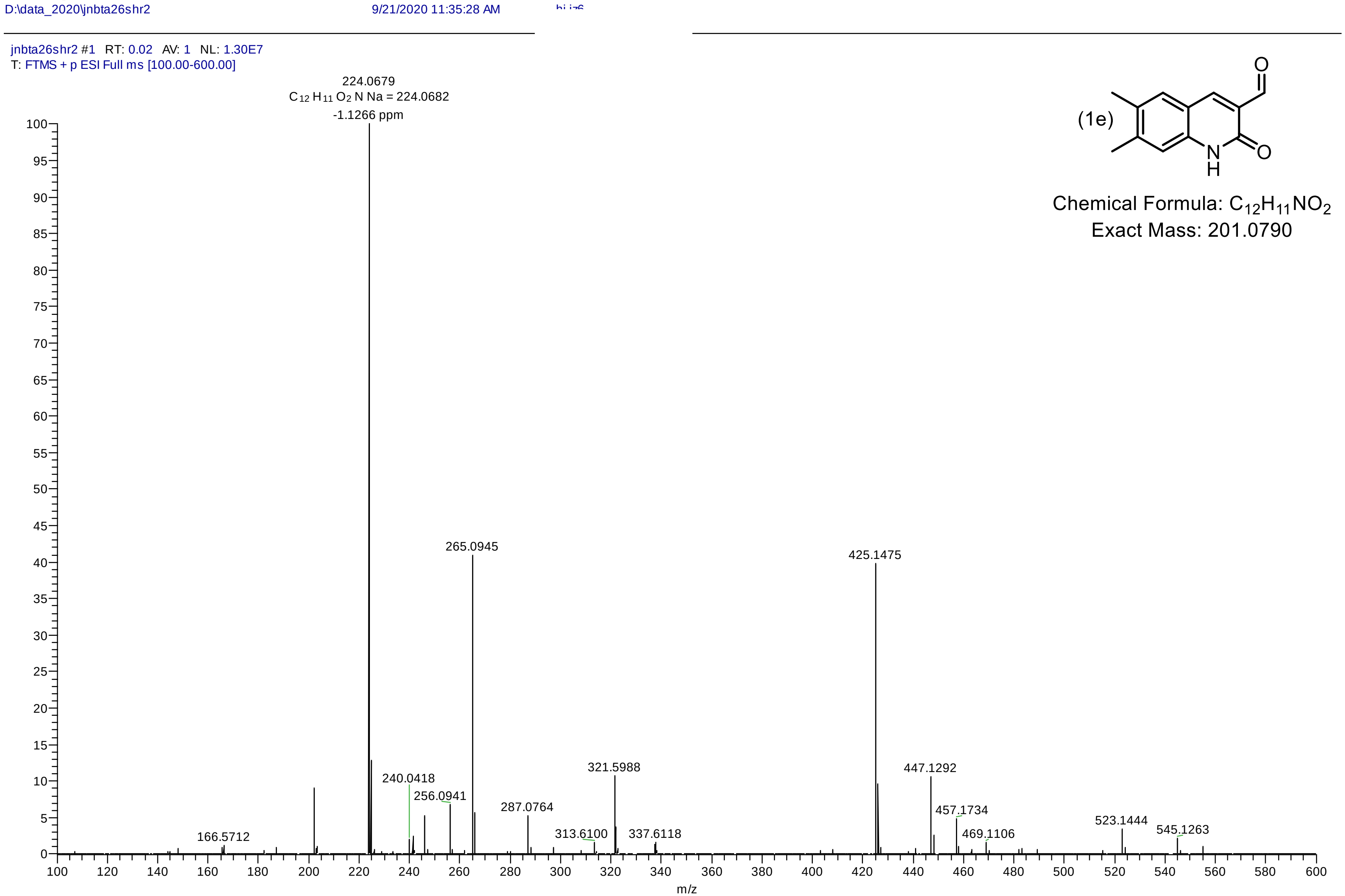


Figure S29. HRMS-ESI 1e.

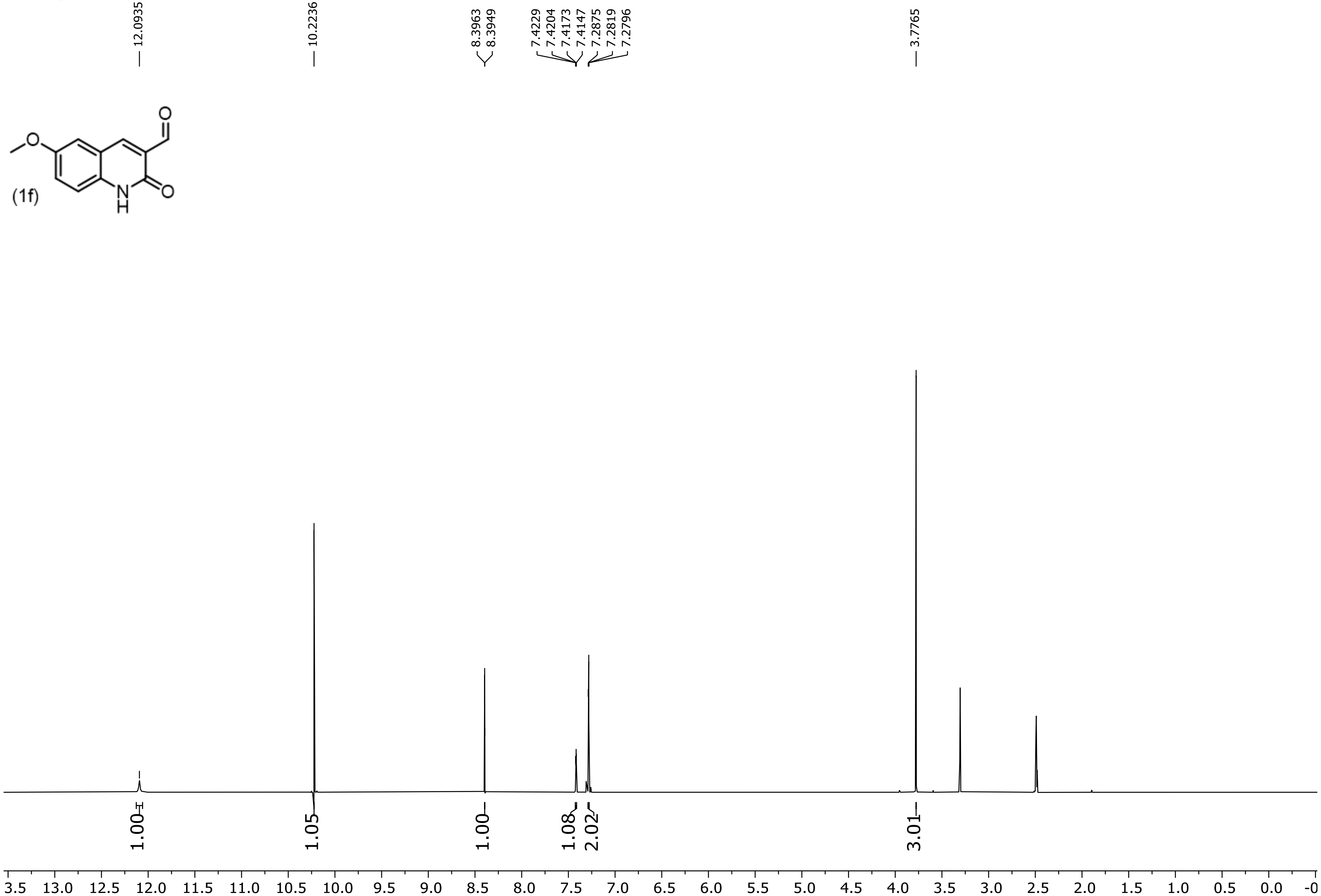
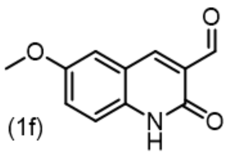


Figure S30. ^{1}H NMR 1f.


(1f)

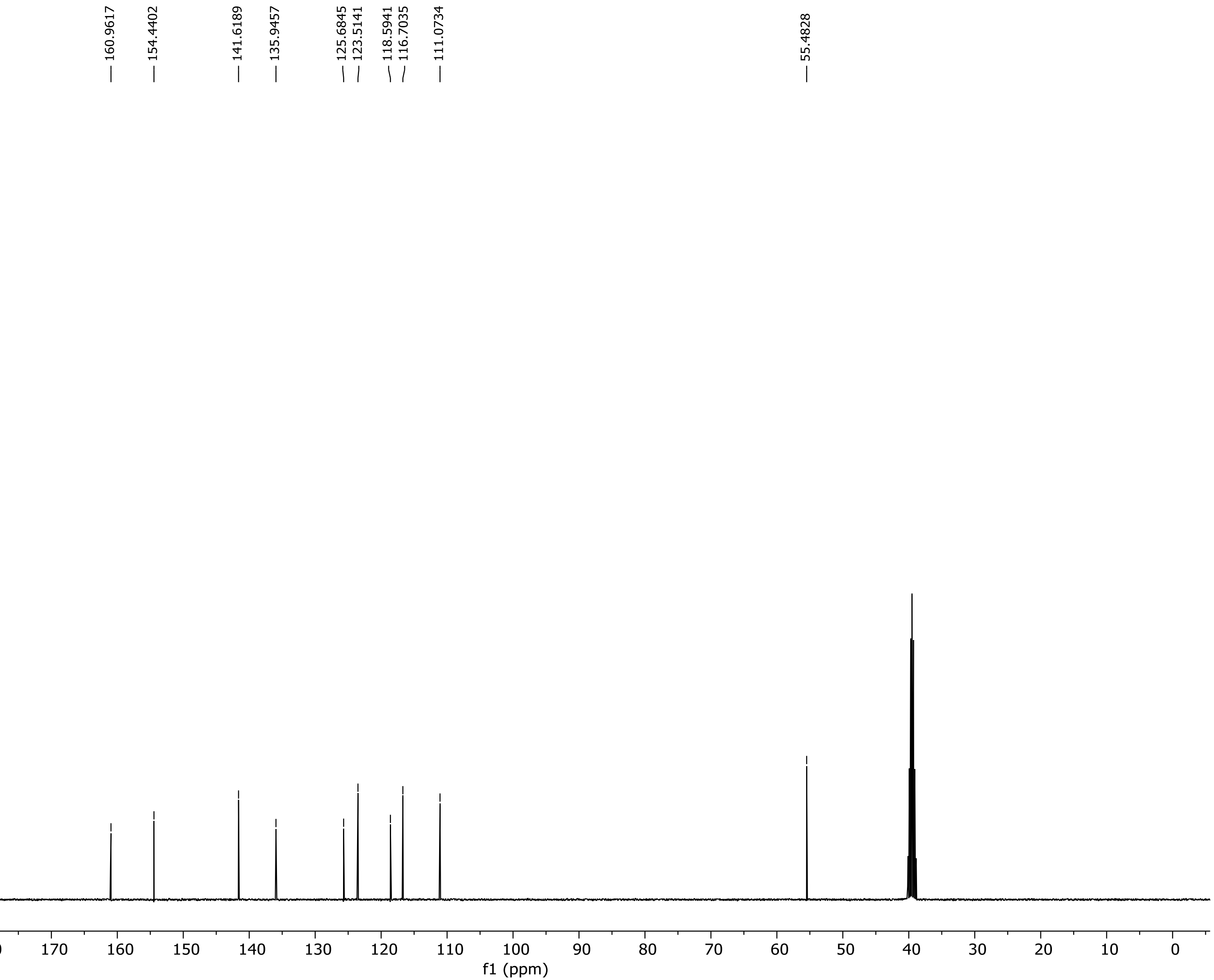
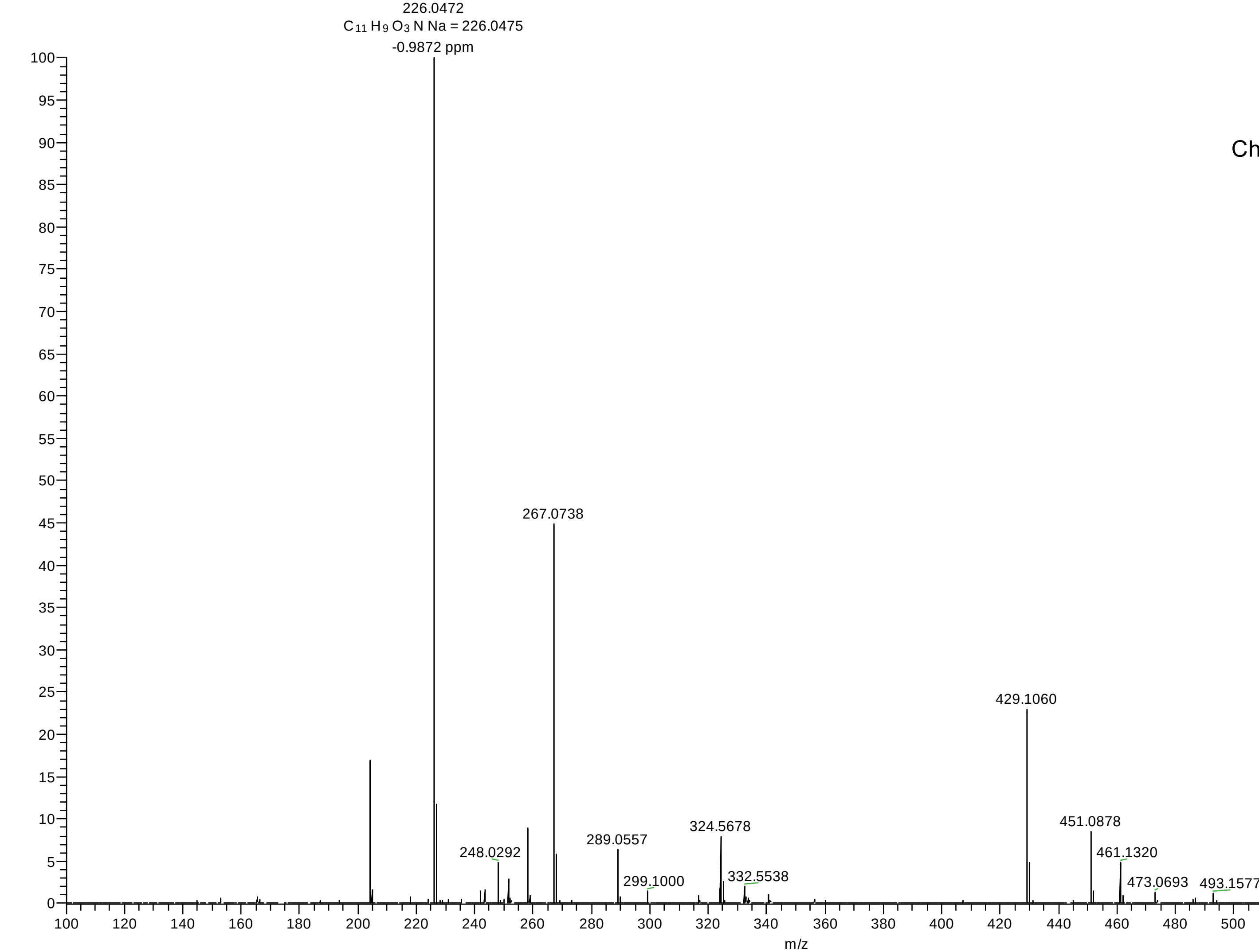
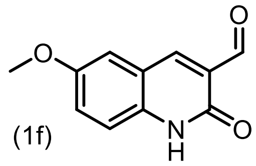


Figure S31. ^{13}C NMR 1f.





(1f)

Chemical Formula: $C_{11}H_9NO_3$

Exact Mass: 203.0582

Figure S32. HRMS-ESI 1f.

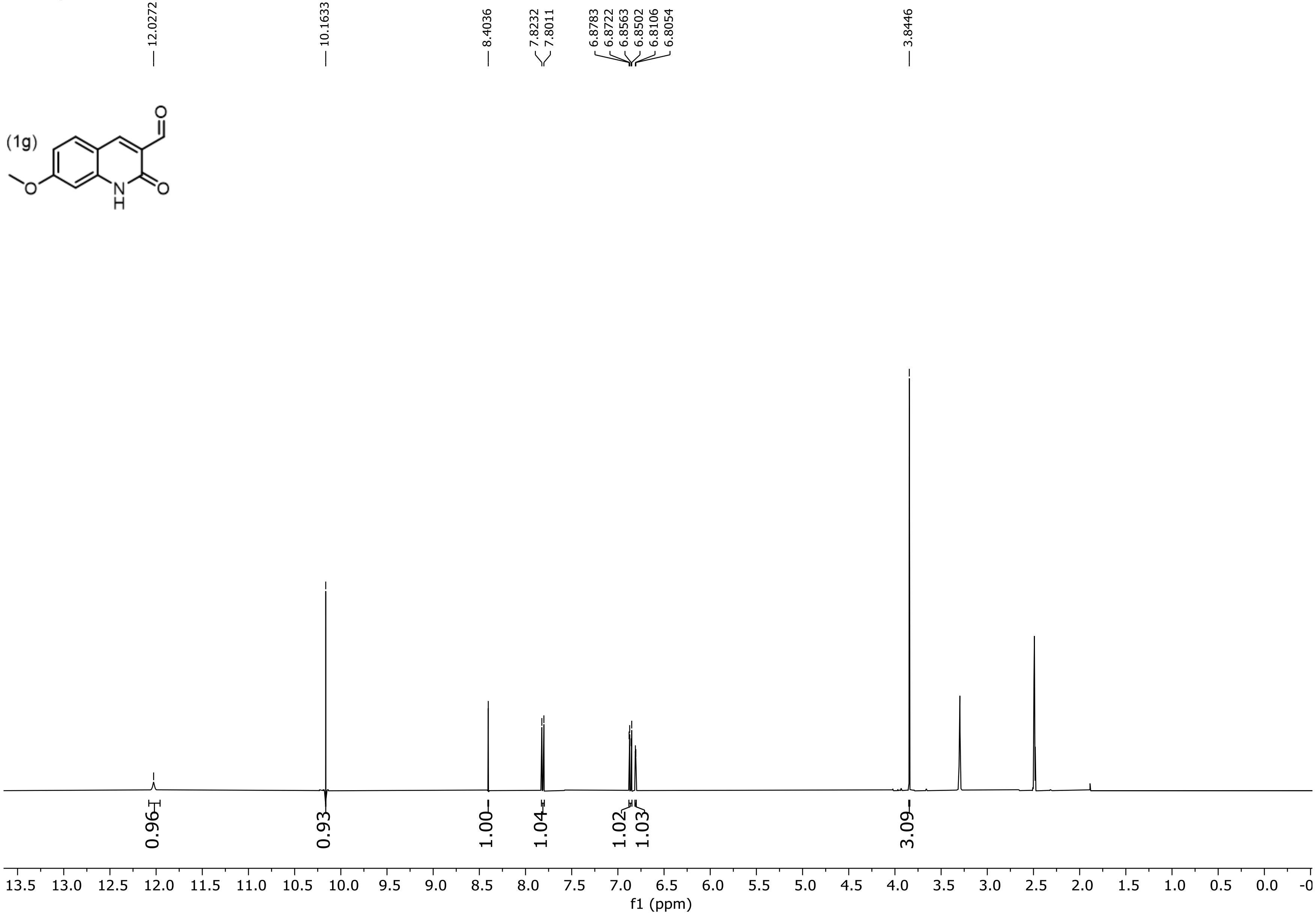
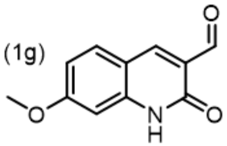


Figure S33. ^{1}H NMR 1g.

(1g)



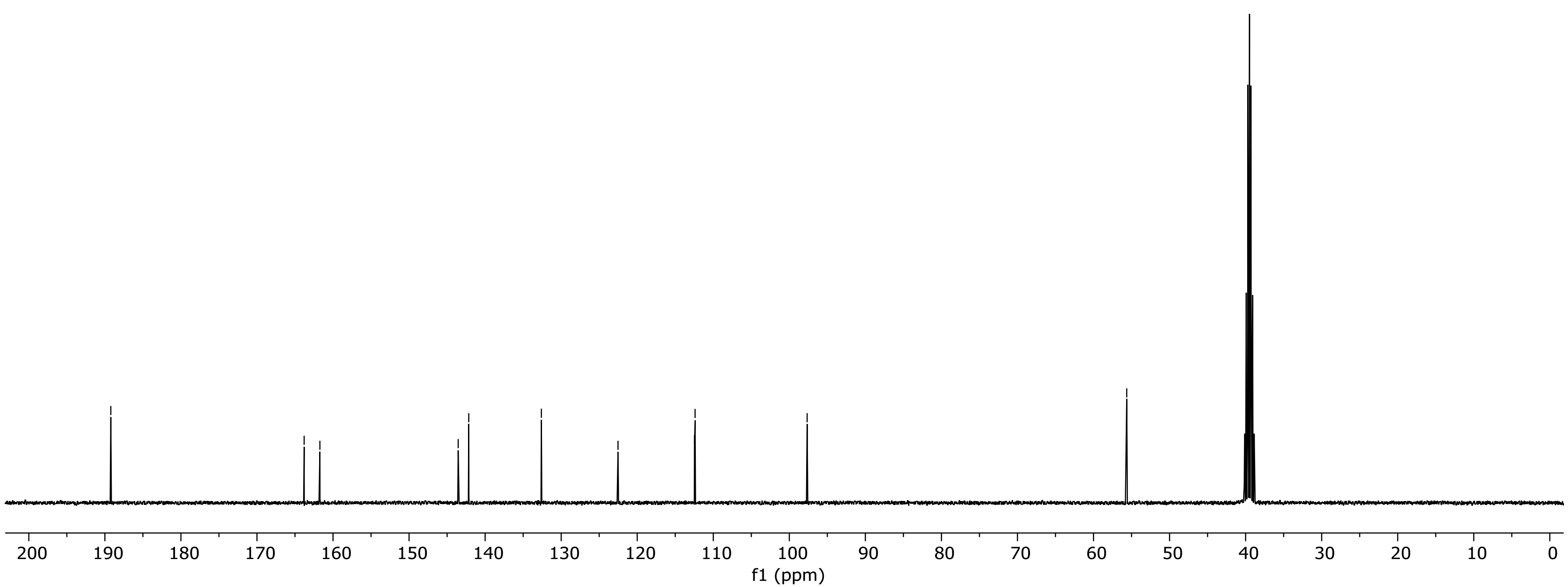
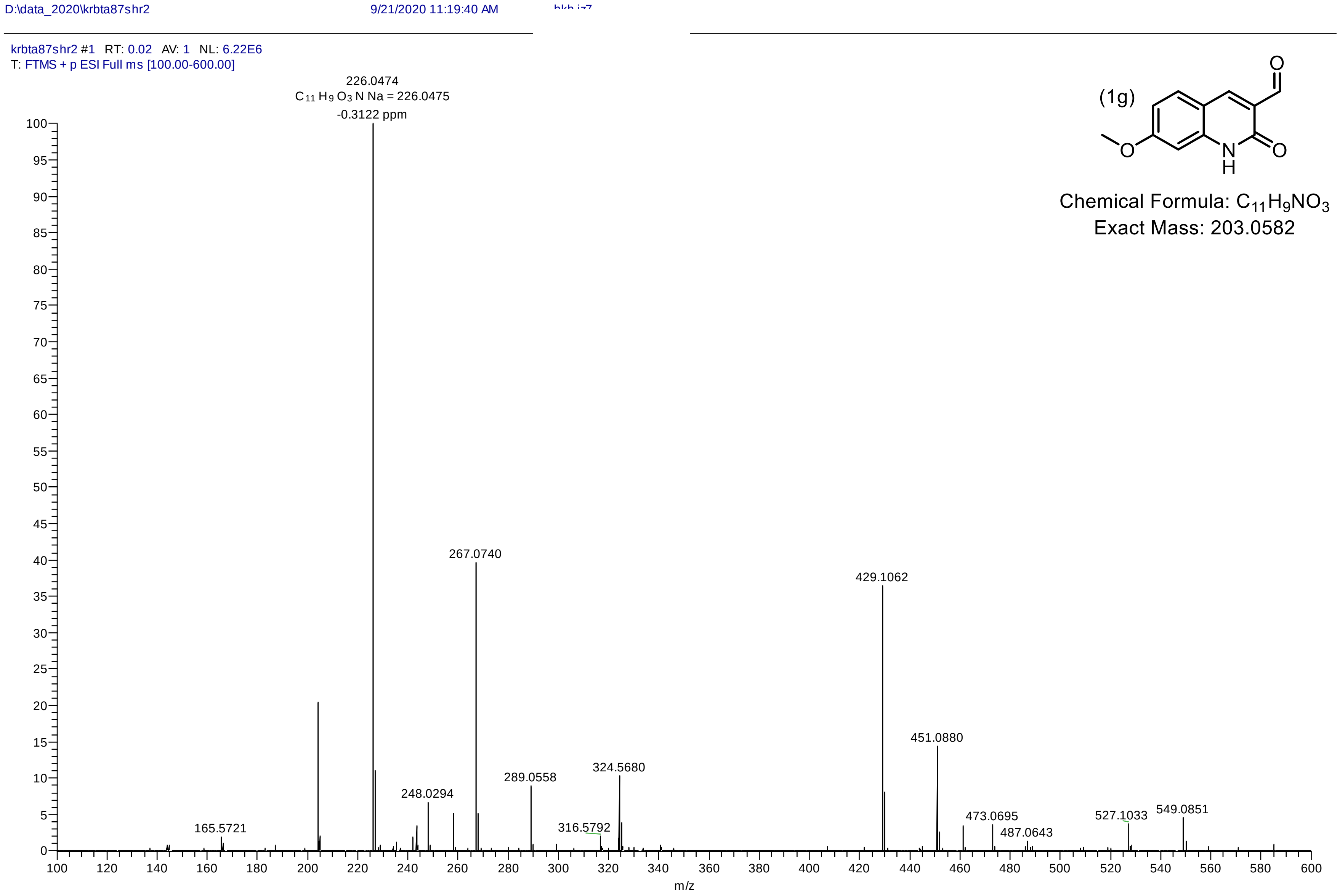
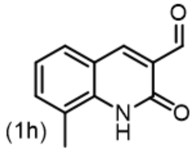


Figure S34. ^{13}C NMR 1g.



Chemical Formula: $C_{11}H_9NO_3$
Exact Mass: 203.0582

Figure S35. HRMS-ESI 1g.



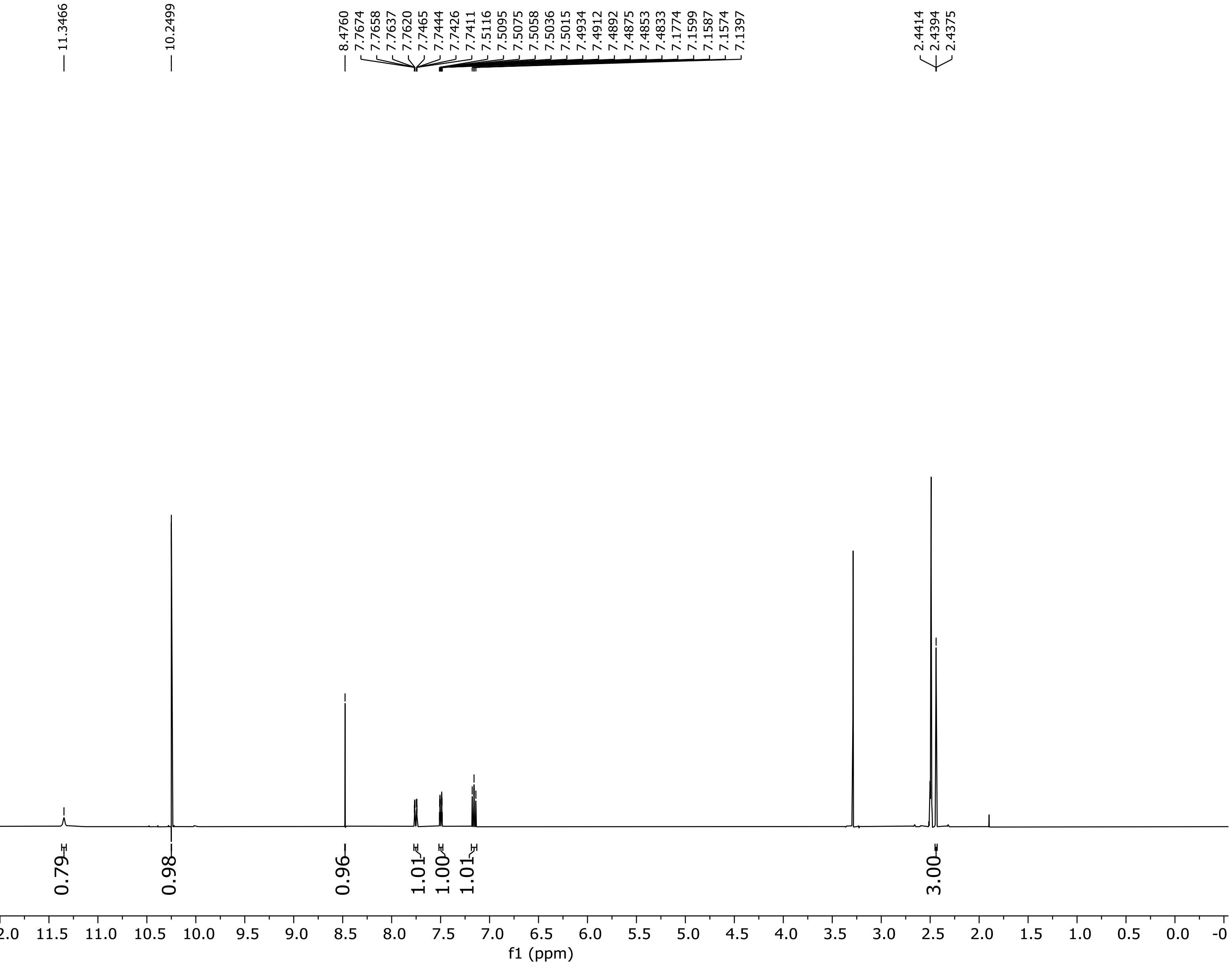


Figure S36. ^{1}H NMR 1h.

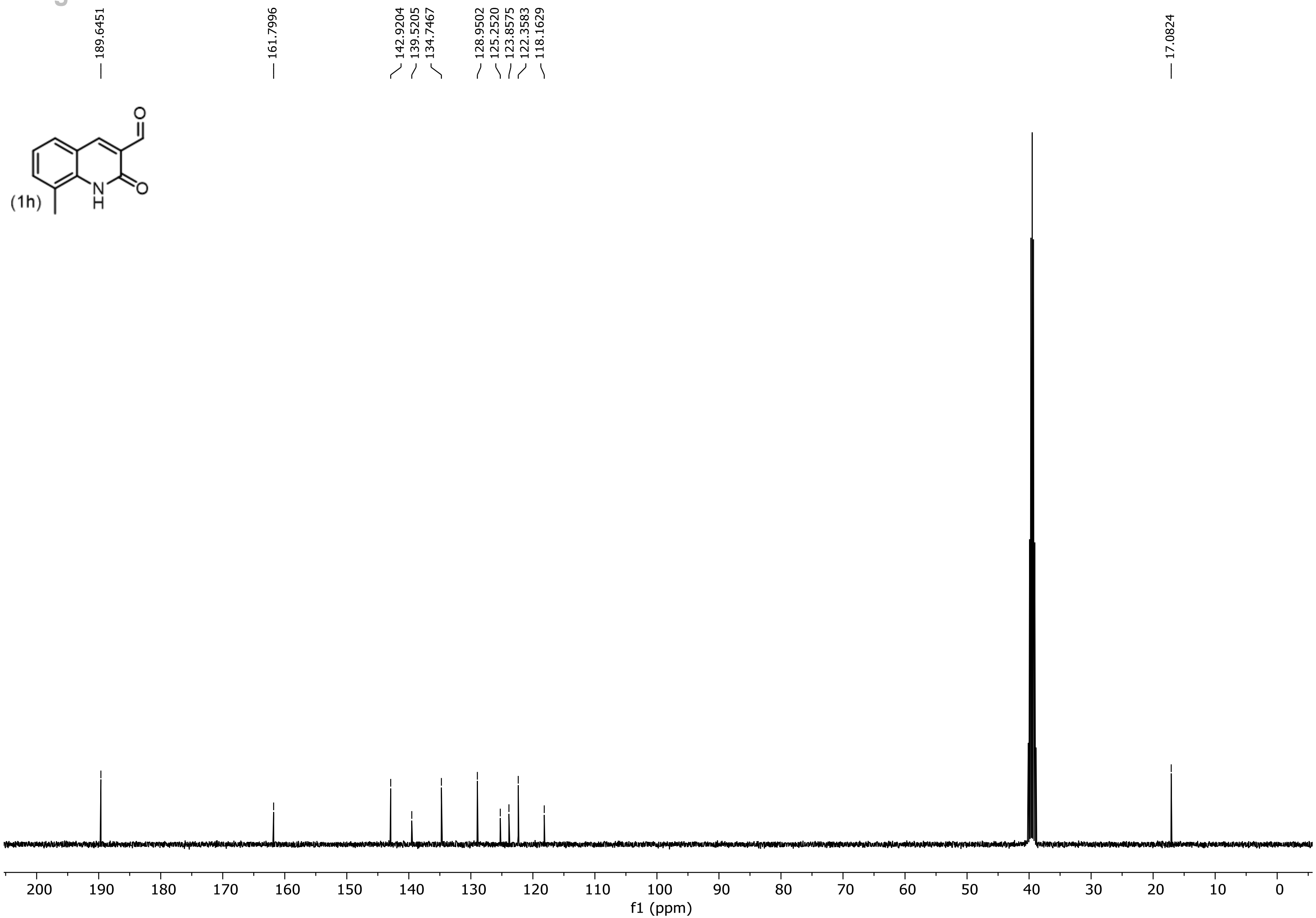


Figure S37. ^{13}C NMR 1h.

D:\data_2020\krbta88shr1 9/21/2020 11:22:15 AM

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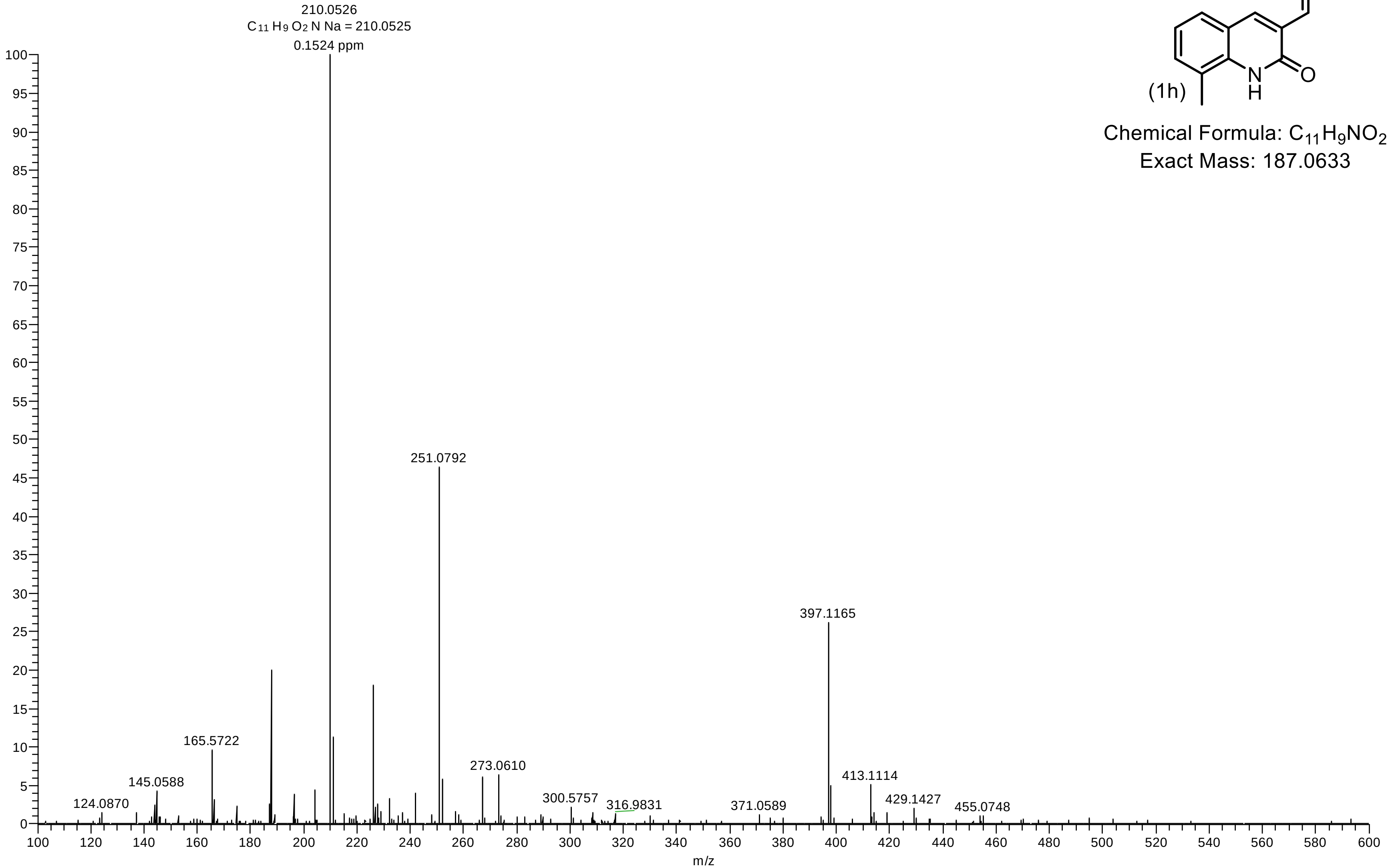


(1h)

Chemical Formula: $C_{11}H_9NO_2$
Exact Mass: 187.0633

Figure S38. HRMS-ESI 1h.

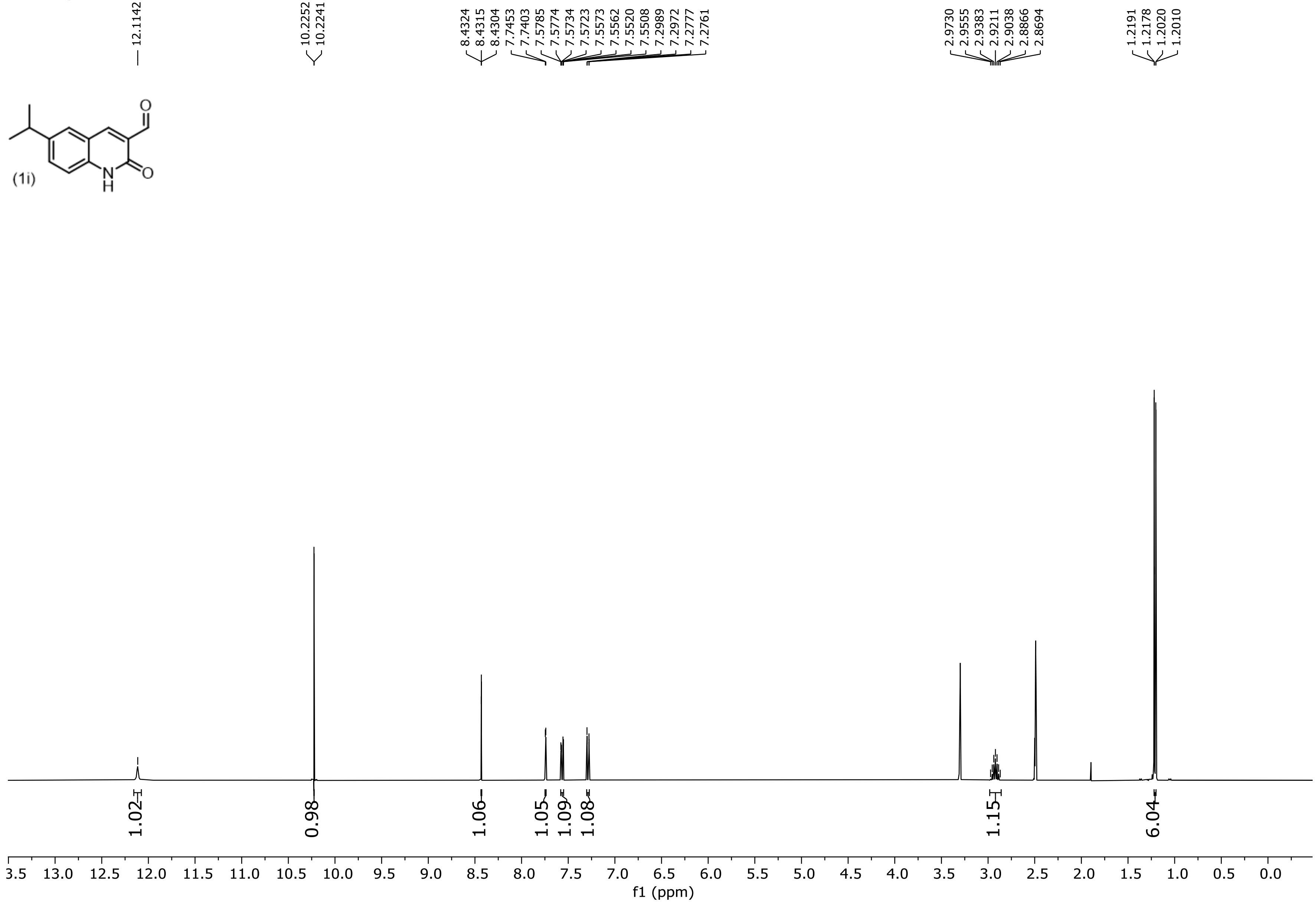


Figure S39. ^{1}H NMR 1i.

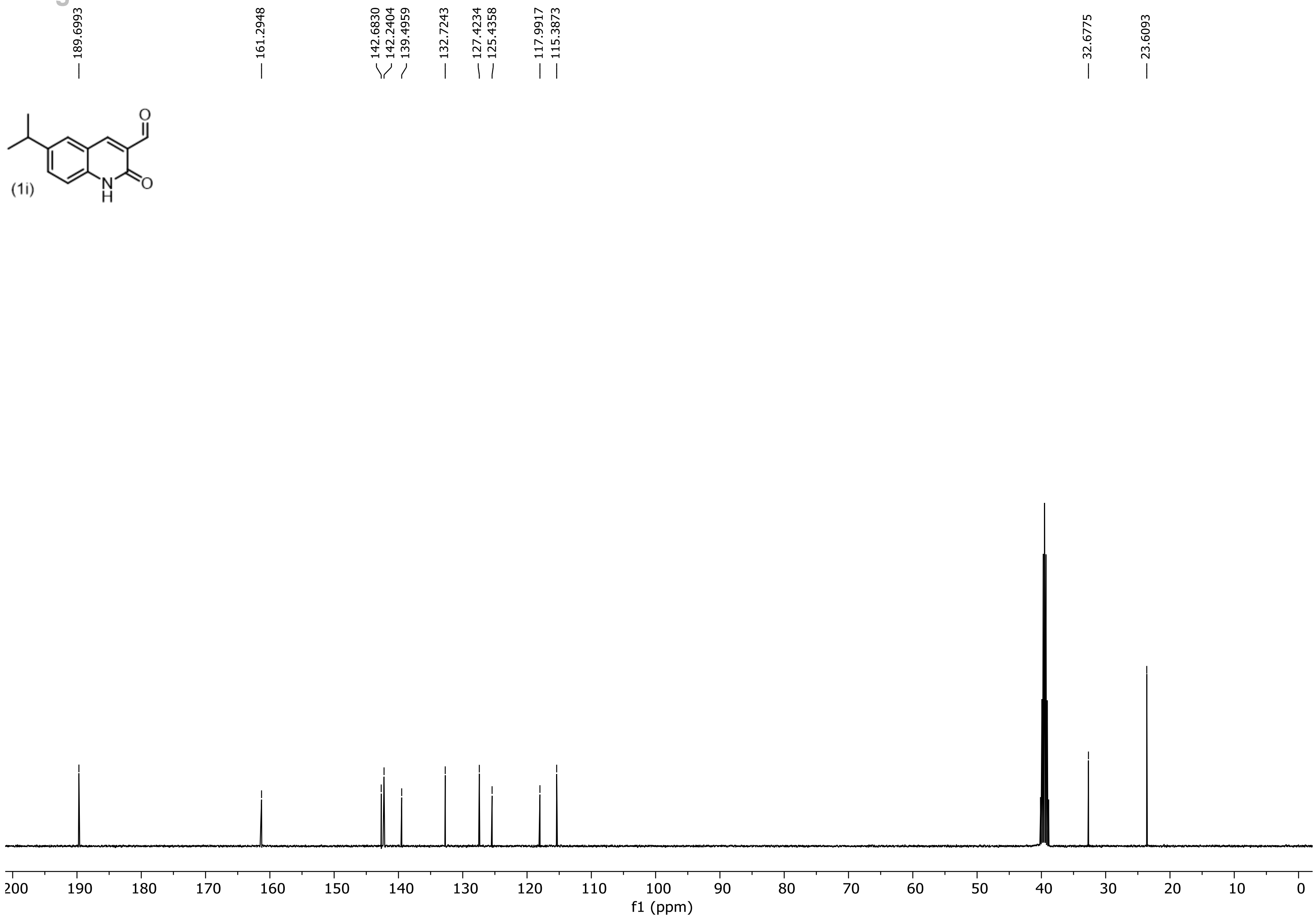
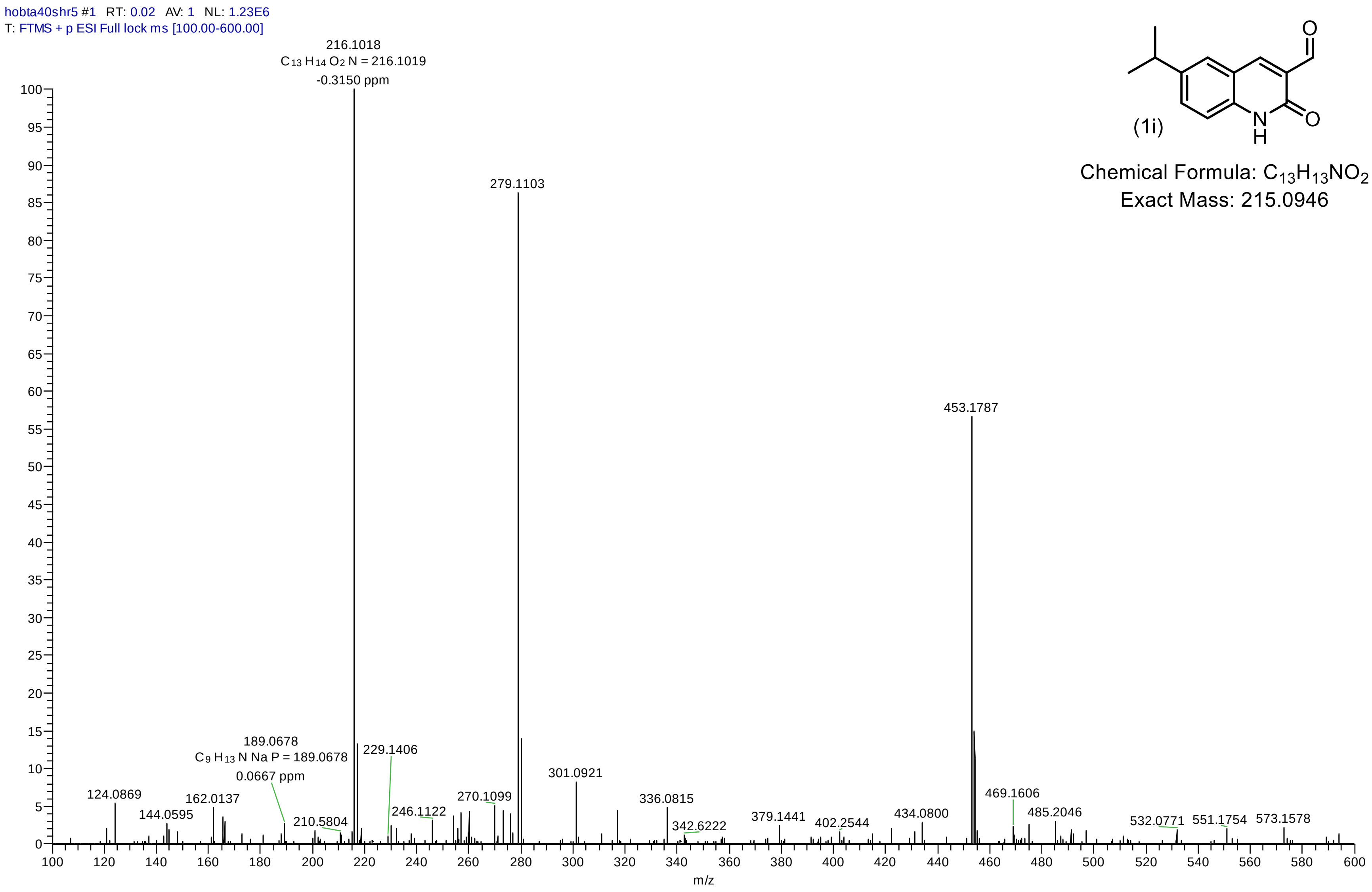


Figure S40. ^{13}C NMR 1i.

D:\data_2020\hobta40shr5 9/22/2020 2:26:02 PM



(1i)

Chemical Formula: $C_{13}H_{13}NO_2$
Exact Mass: 215.0946

Figure S41. HRMS-ESI 1i.

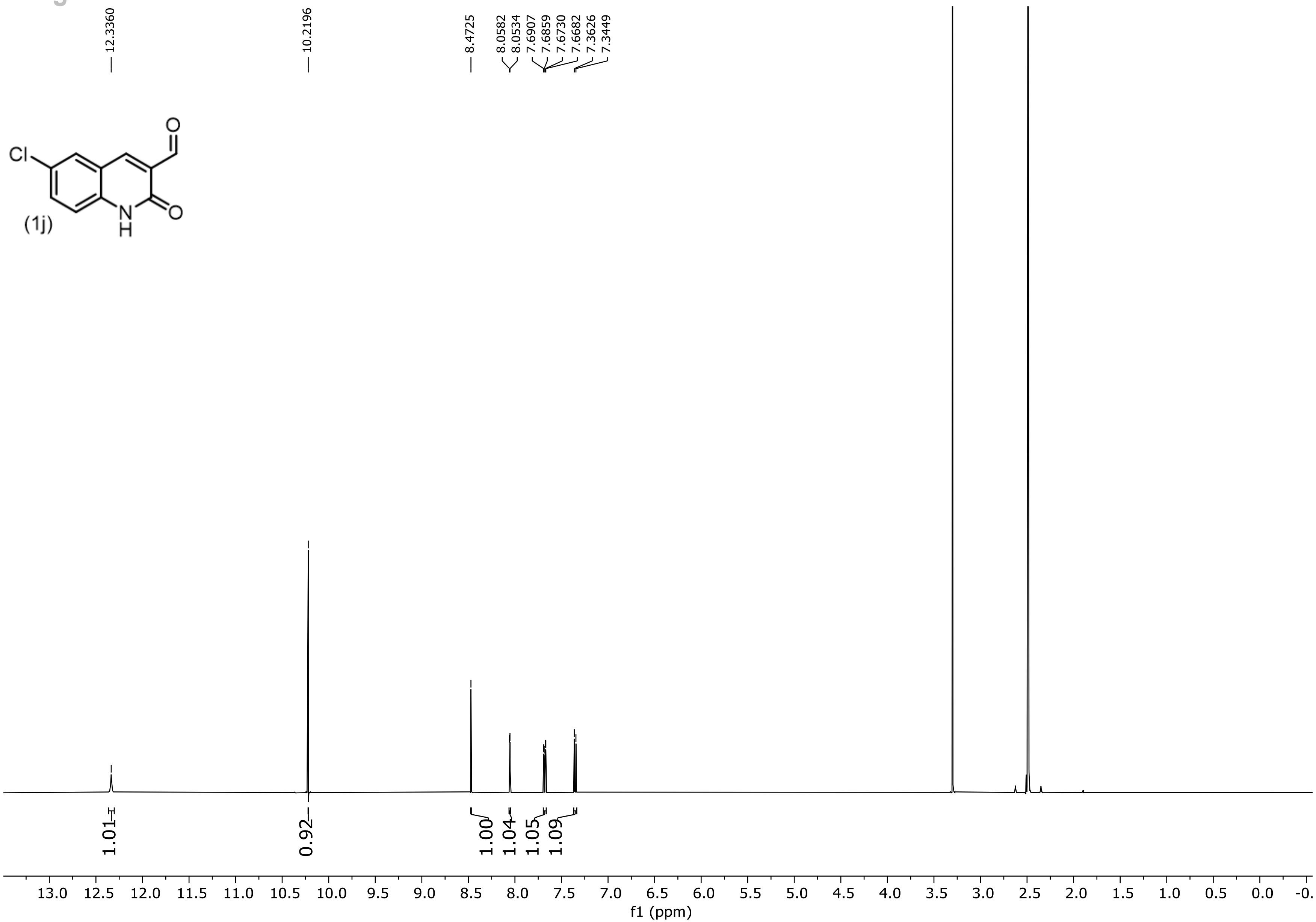


Figure S42. ^1H NMR 1j.

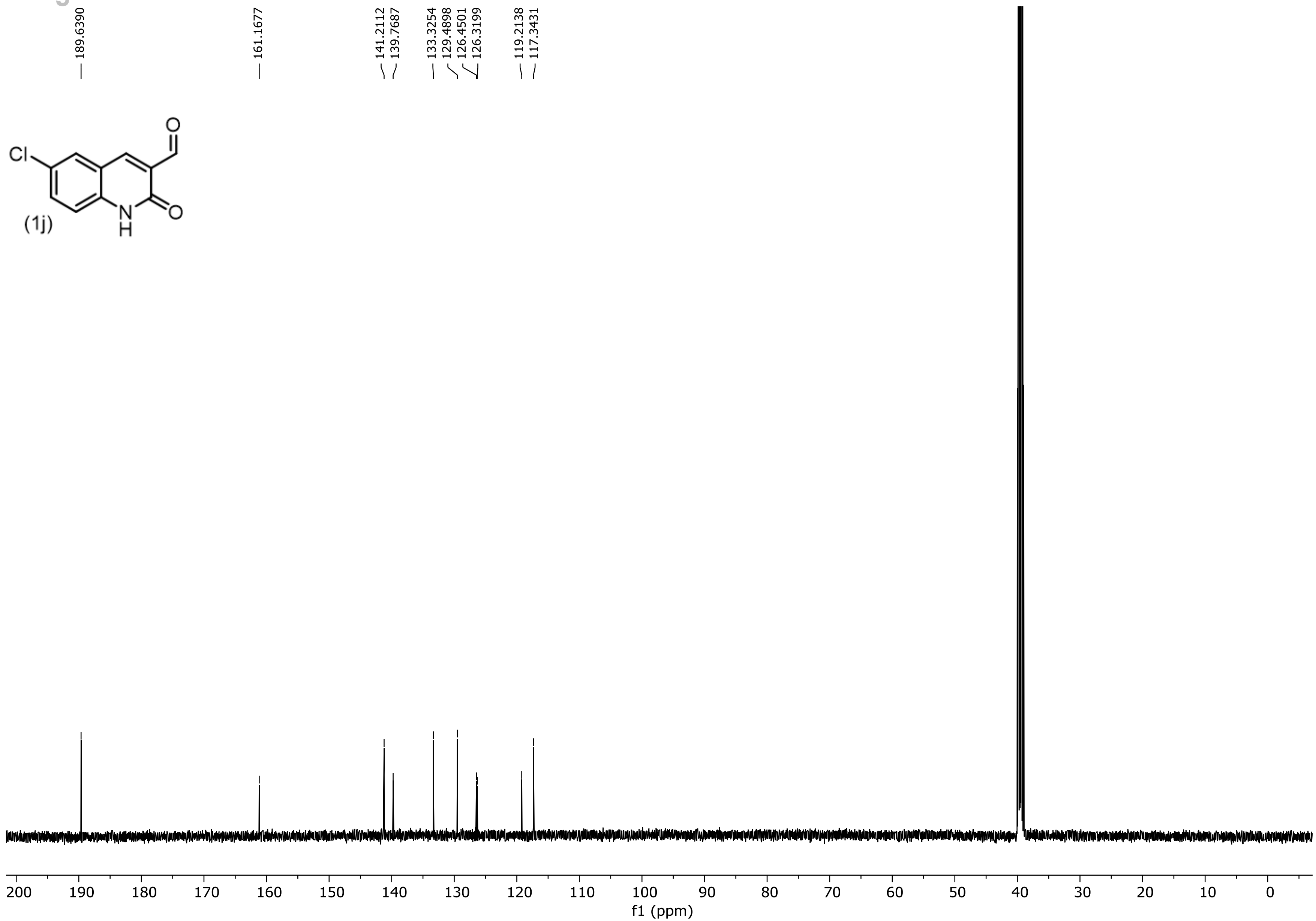
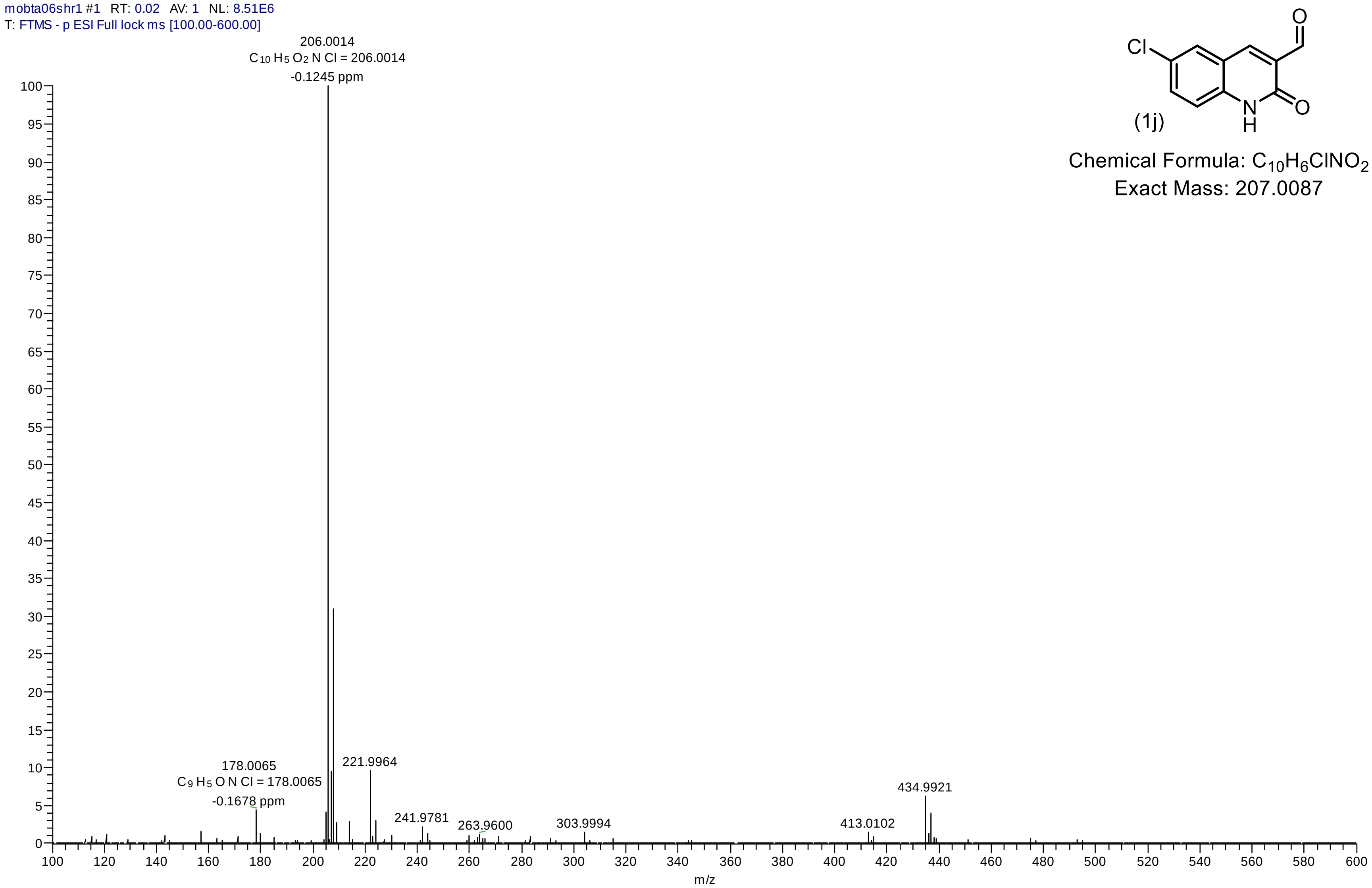


Figure S43. ^{13}C NMR 1j.

D:\data_2020\mobta06shr1 9/22/2020 2:43:53 PM



(1j)

Chemical Formula: $C_{10}H_6ClNO_2$
Exact Mass: 207.0087

Figure S44. HRMS-ESI 1j.

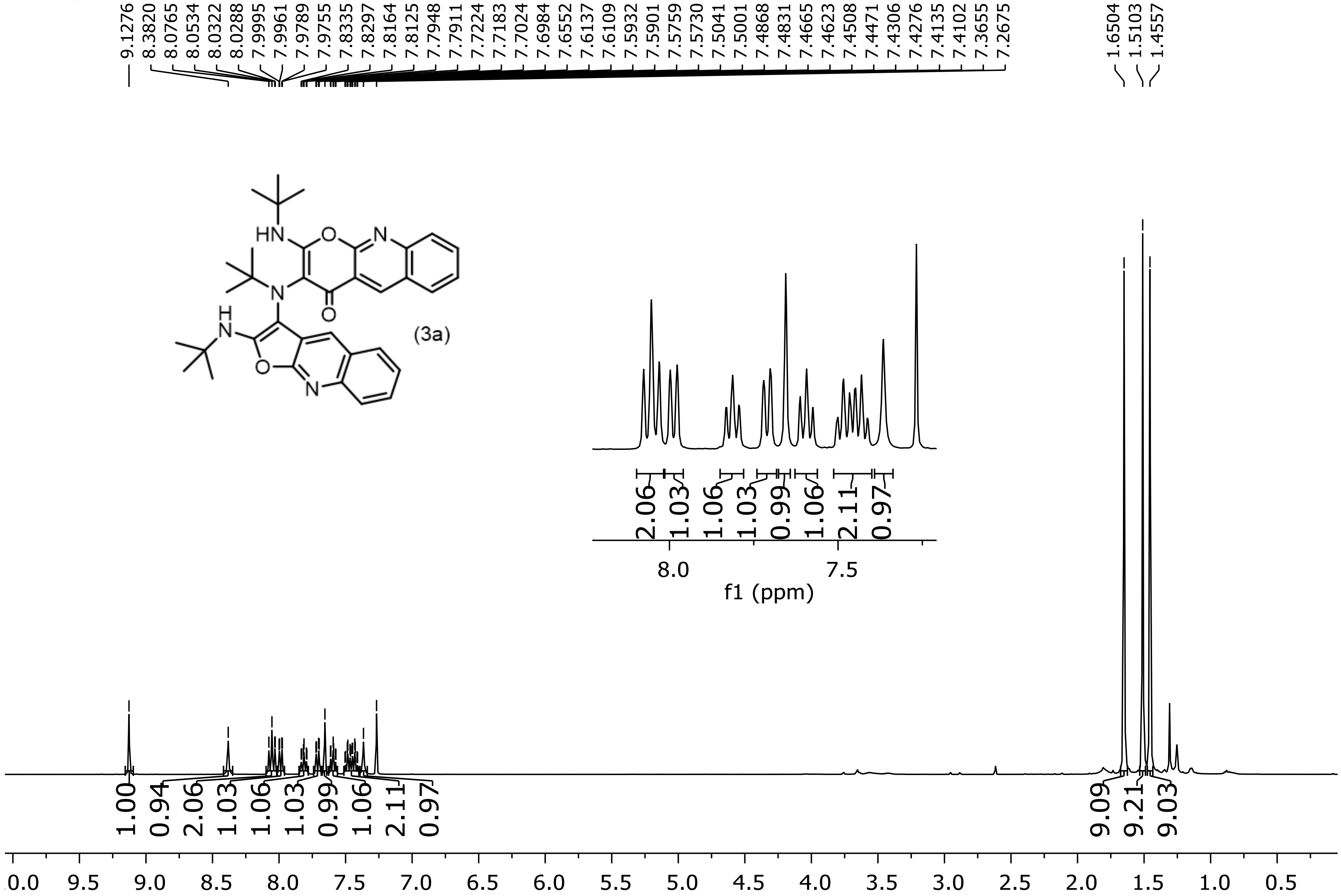


Figure S45. ^{1}H NMR 3a.

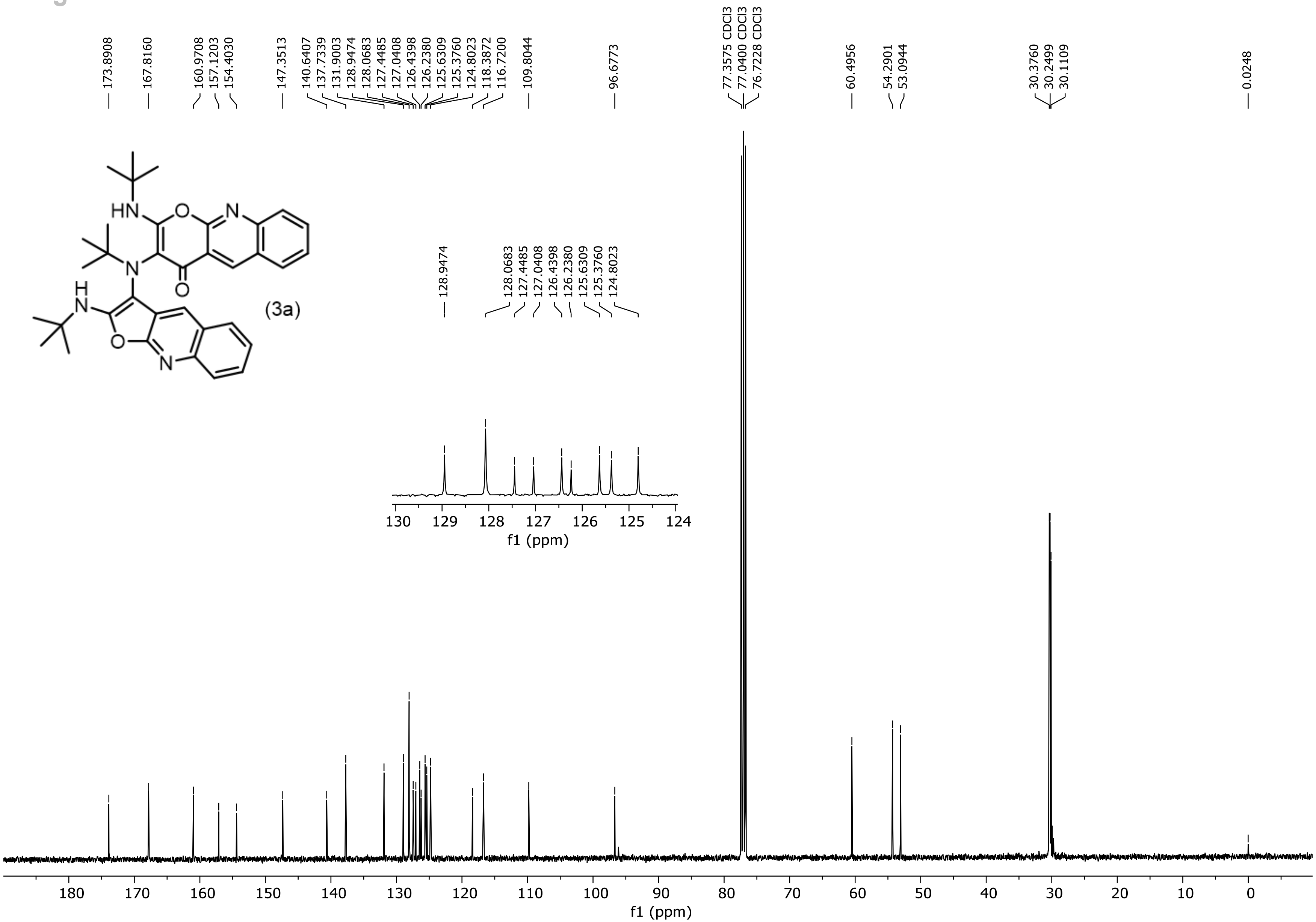


Figure S46. ^{13}C NMR 3a.

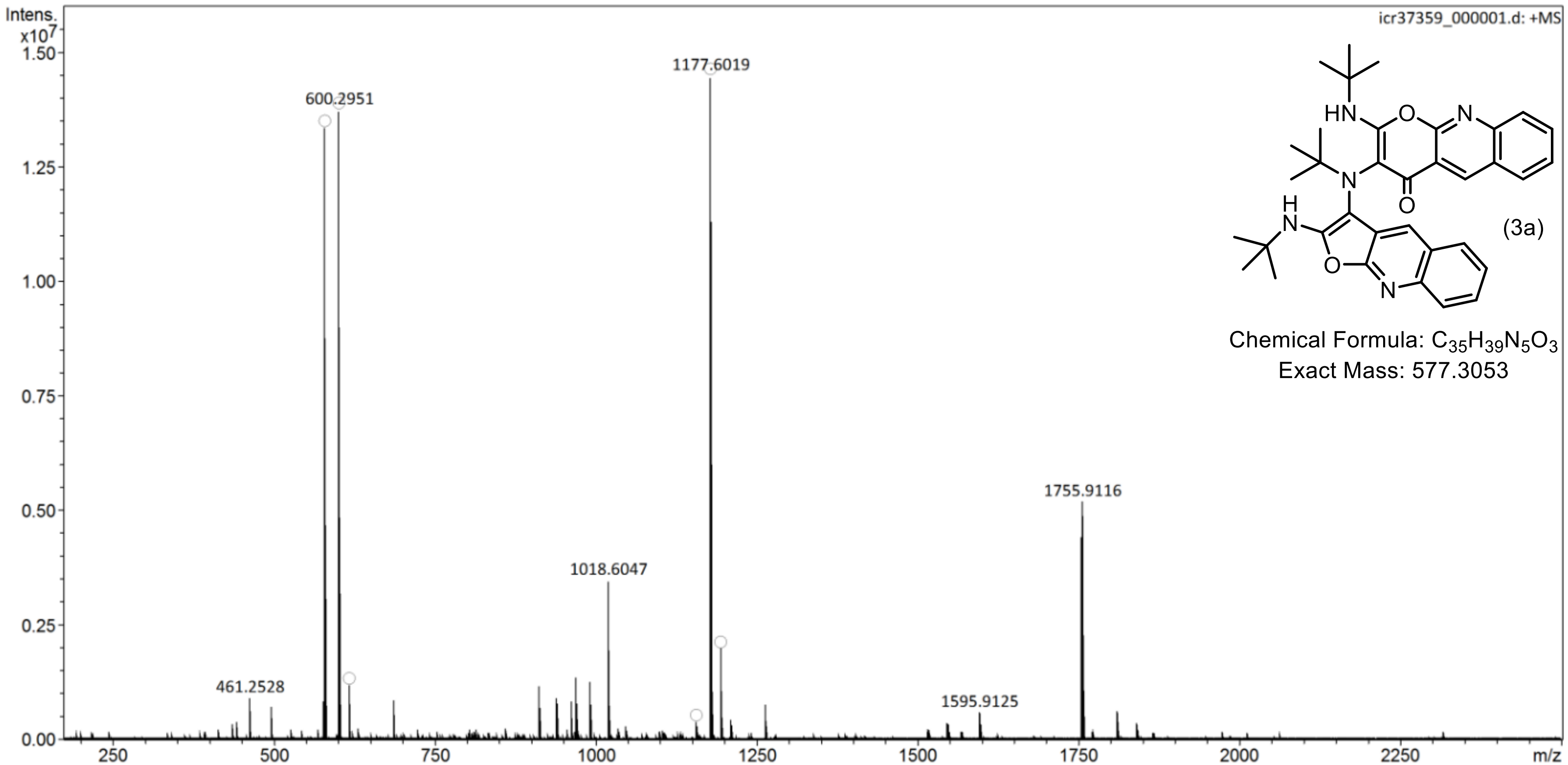


Figure S47. HRMS-ESI 3a.

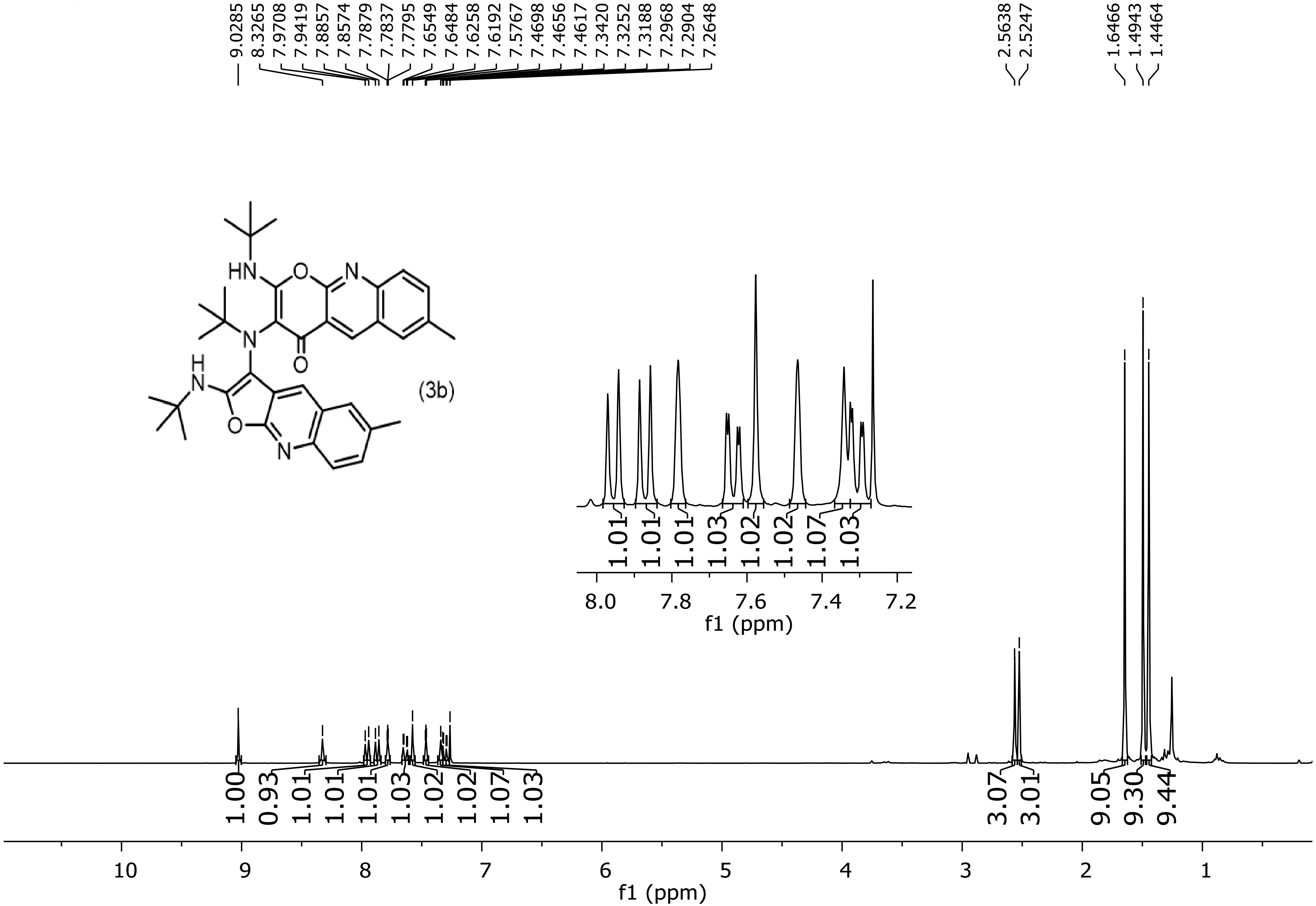


Figure S48. ¹H NMR 3b.

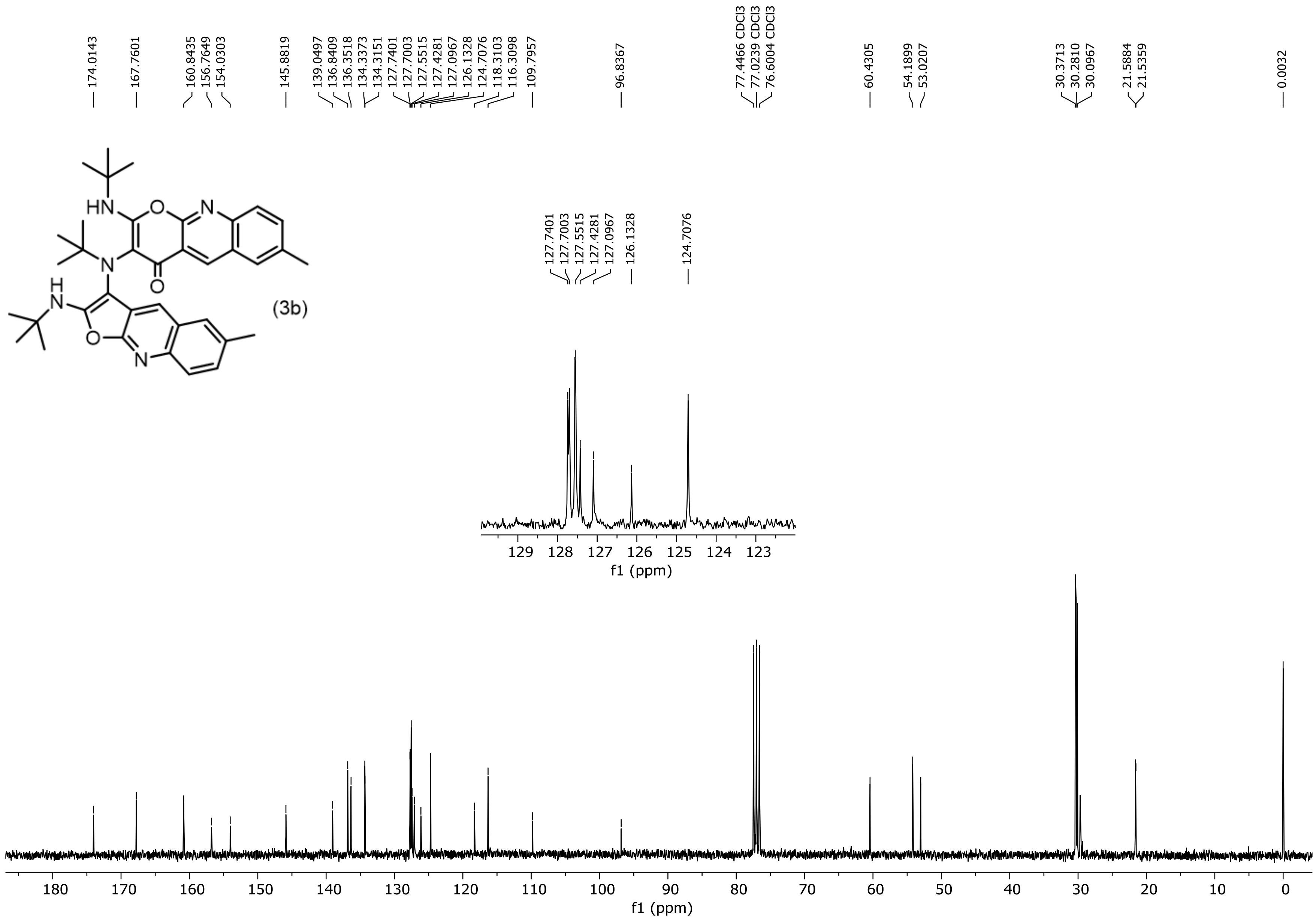

174.0143
167.7601
160.8435
156.7649
154.0303
145.8819
139.0497
136.8409
136.3518
134.3373
134.3151
127.7401
127.7003
127.5515
127.4281
127.0967
126.1328
124.7076
118.3103
116.3098
109.7957
96.8367
77.4466 CDCl3
77.0239 CDCl3
76.6004 CDCl3
60.4305
54.1899
53.0207
30.3713
30.2810
30.0967
21.5884
21.5359
0.0032
HN
O
N
N
O
H
N
O
N
(3b)
f1 (ppm)
f1 (ppm)

Figure S49. ^{13}C NMR 3b.

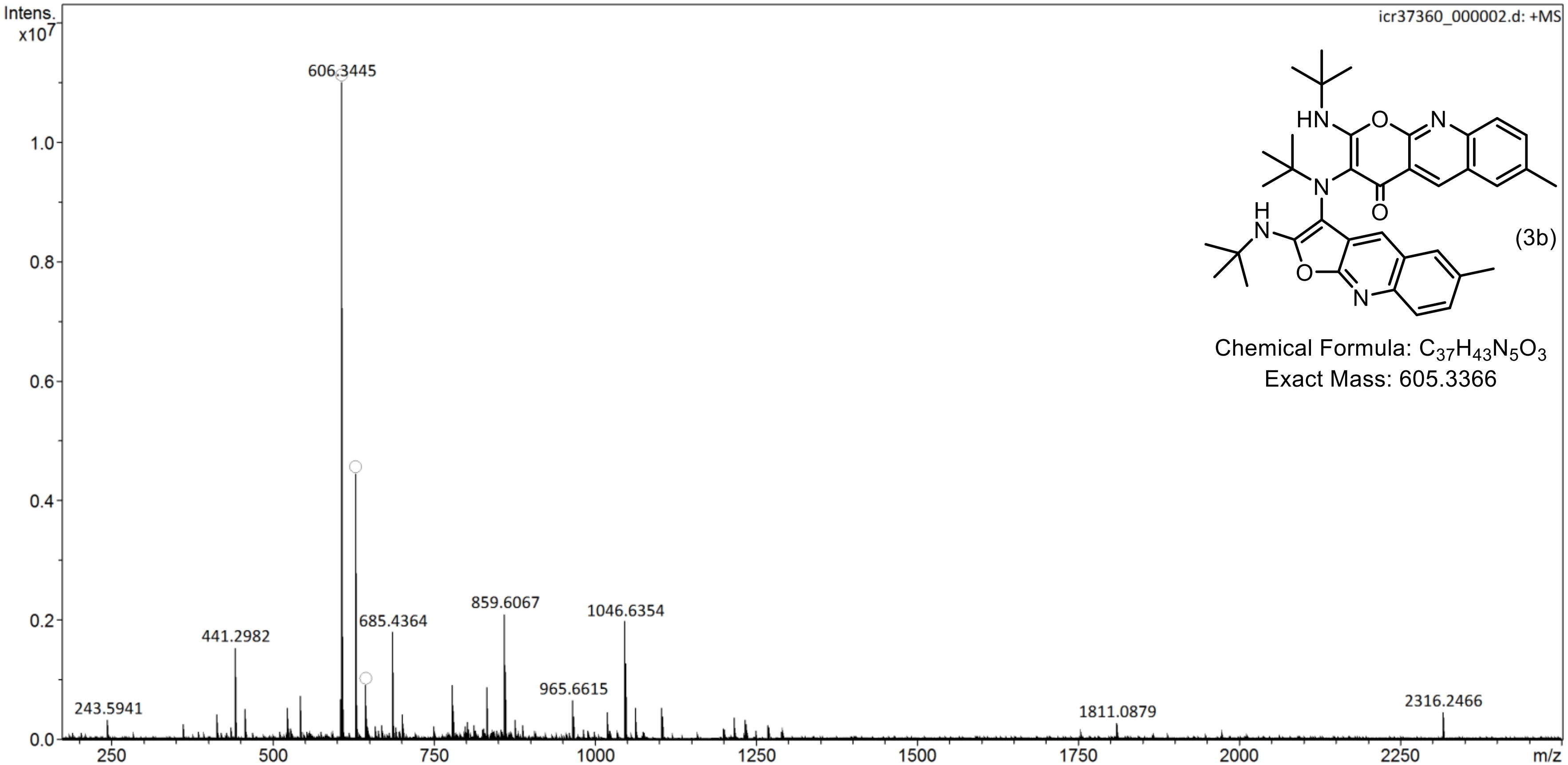
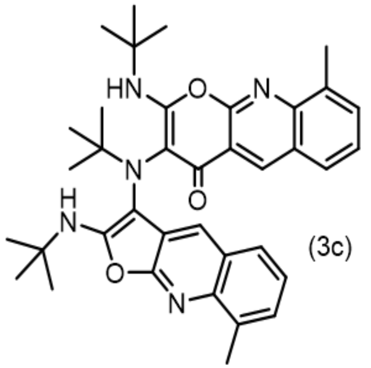


Figure S50. HRMS-ESI 3b.



(3c)

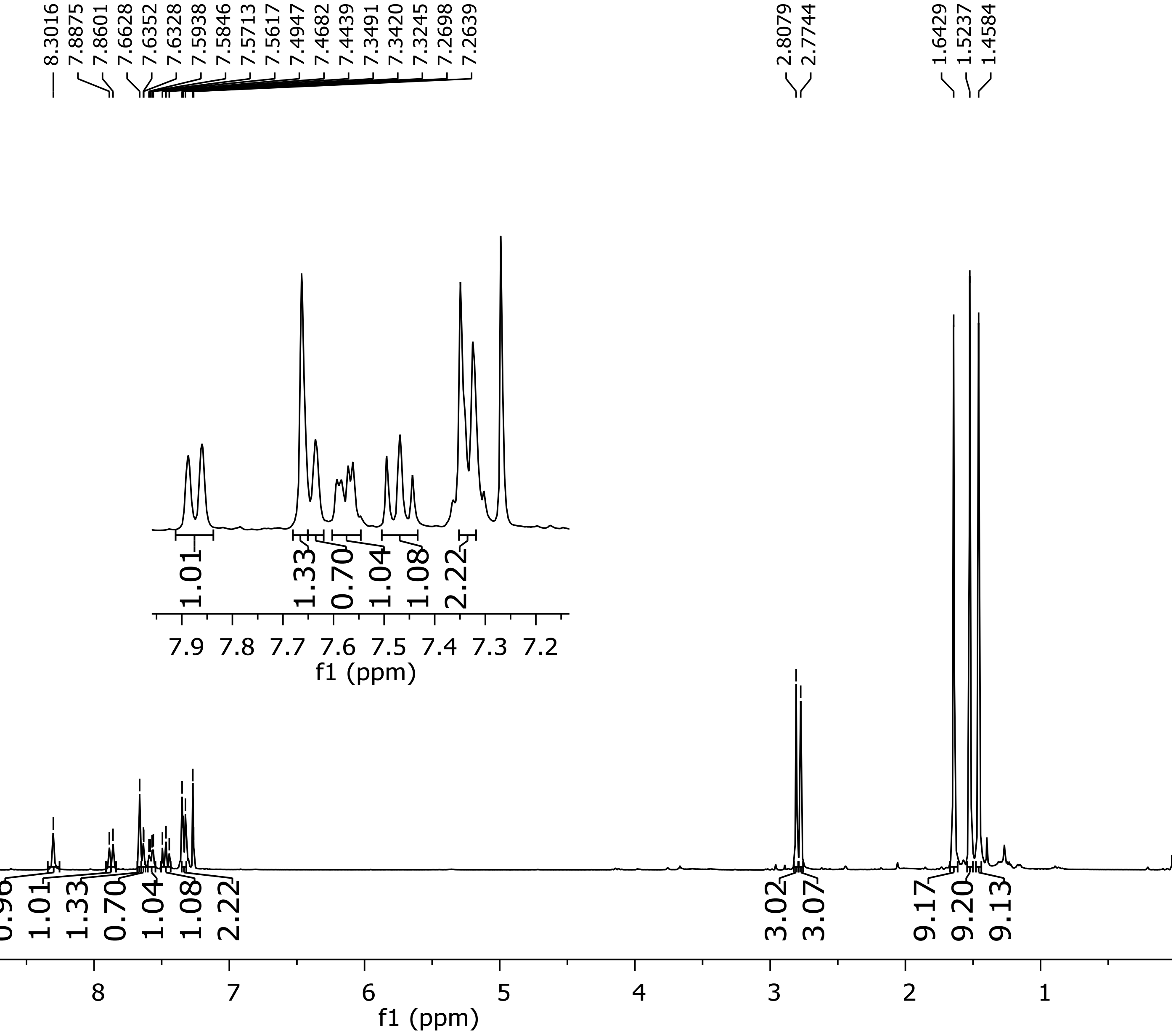


Figure S51. ^{1}H NMR 3c.

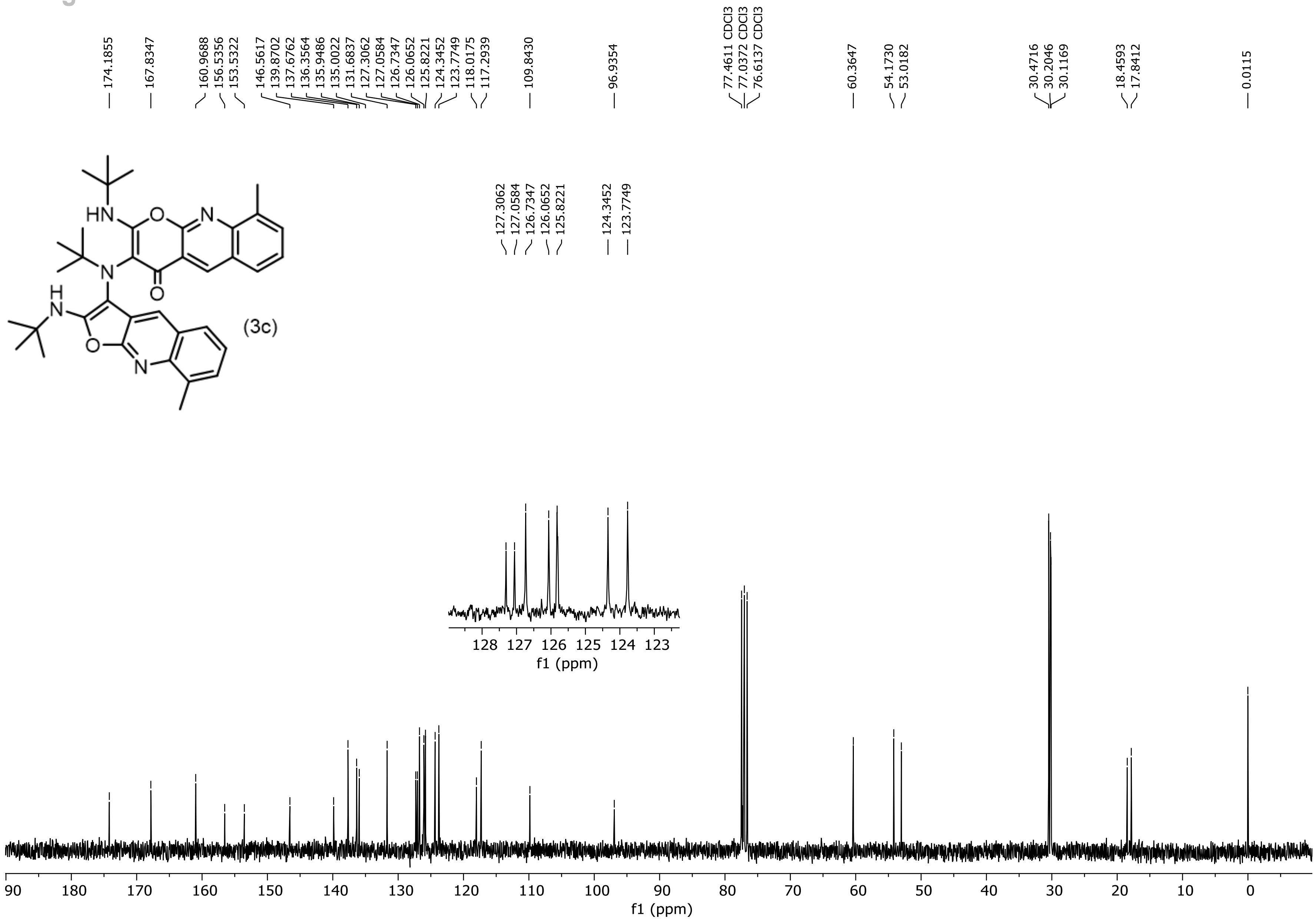
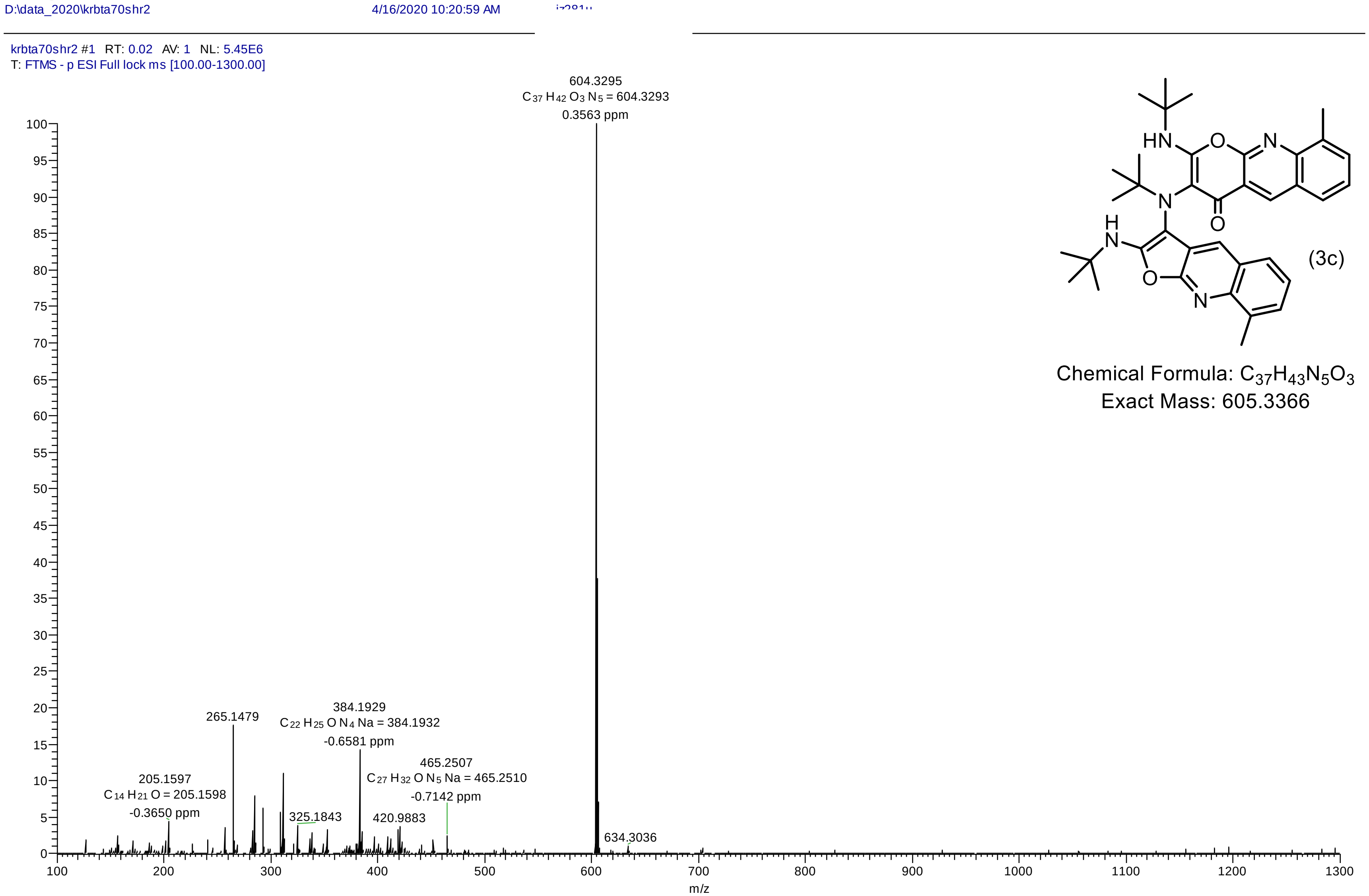


Figure S52. ^{13}C NMR 3c.



(3c)

Chemical Formula: $C_{37}H_{43}N_5O_3$
Exact Mass: 605.3366

Figure S53. HRMS-ESI 3c.

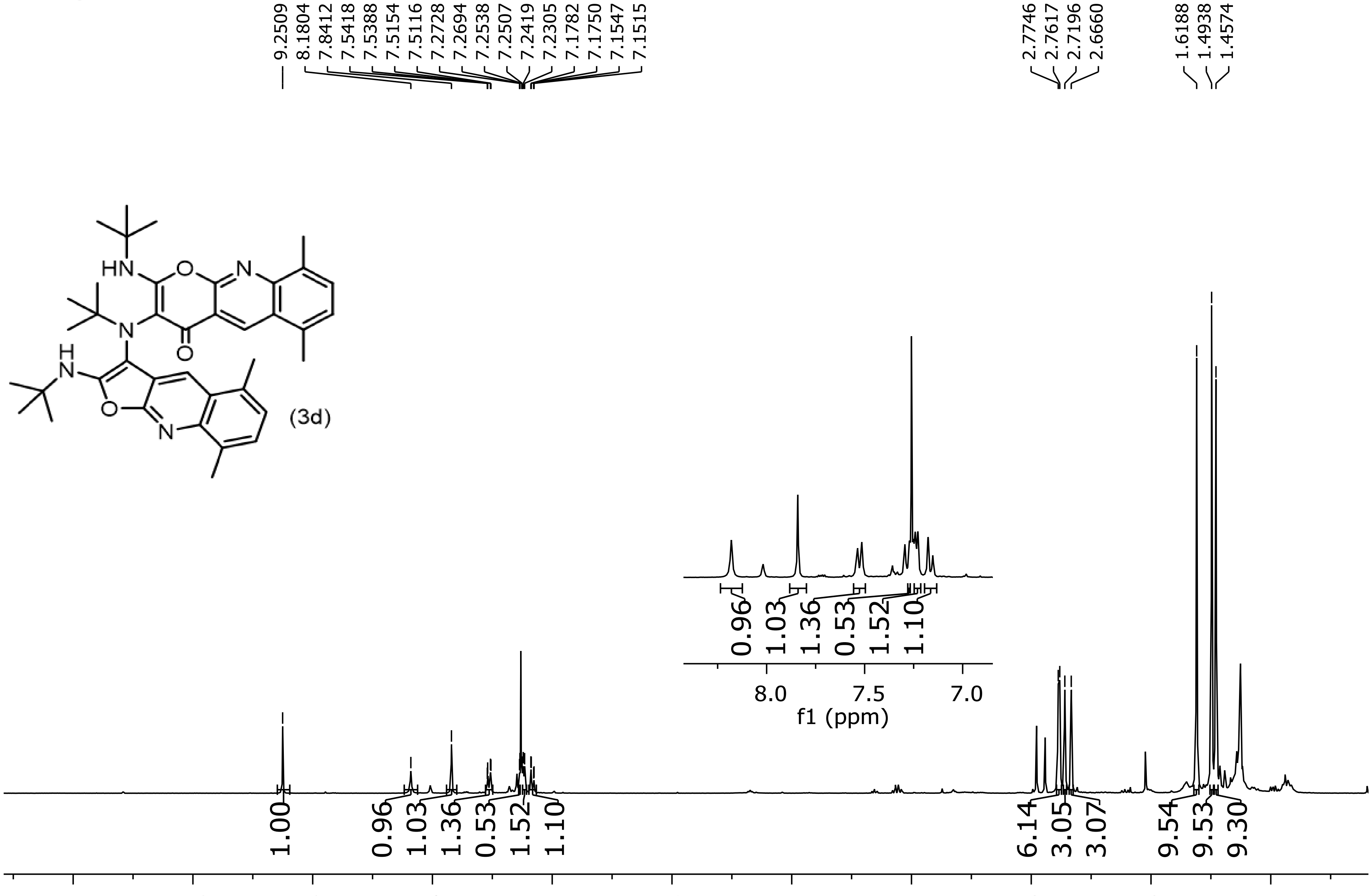


Figure S54. ^{1}**H NMR 3d.**

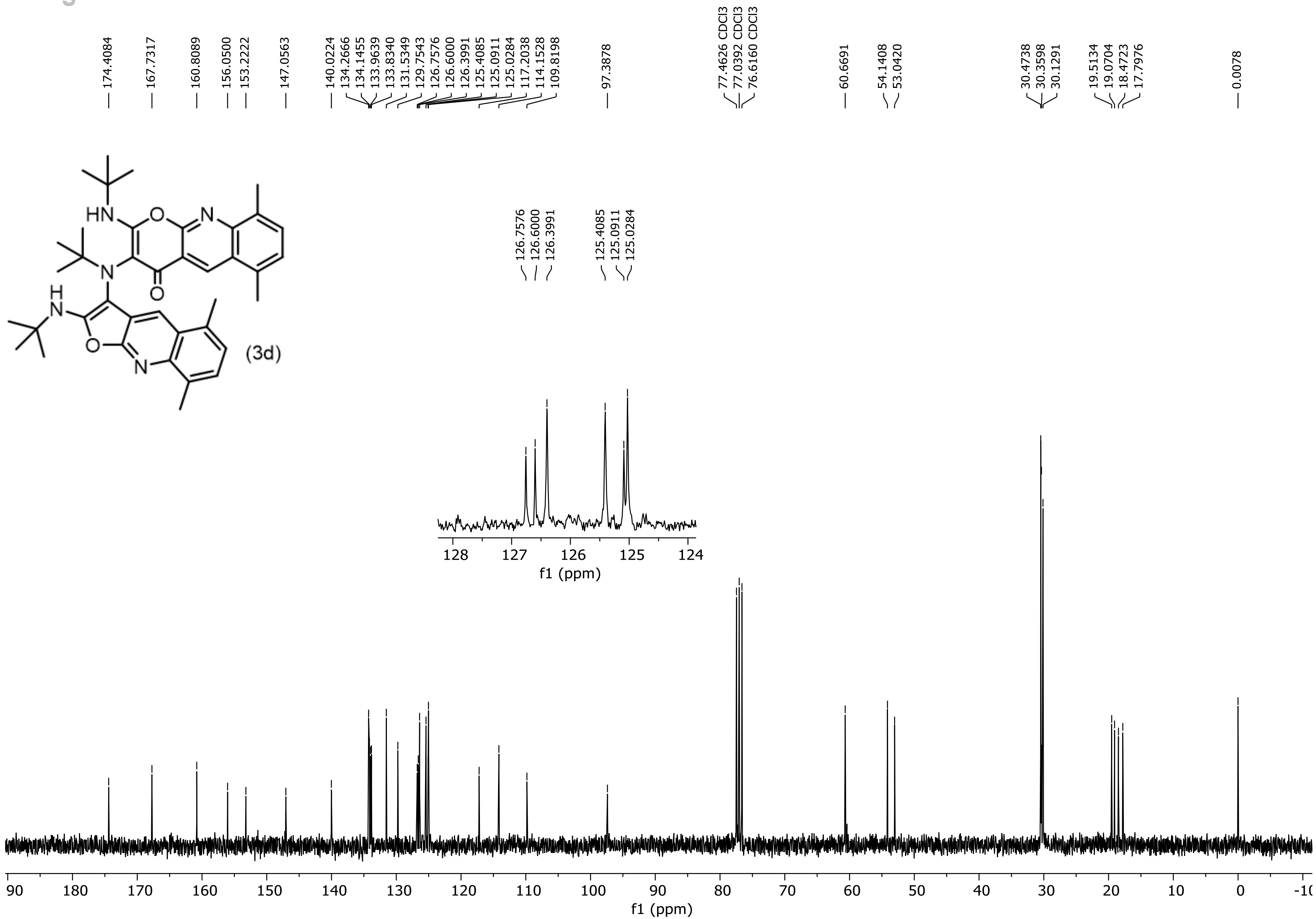


Figure S55. ^{13}**C NMR 3d.**

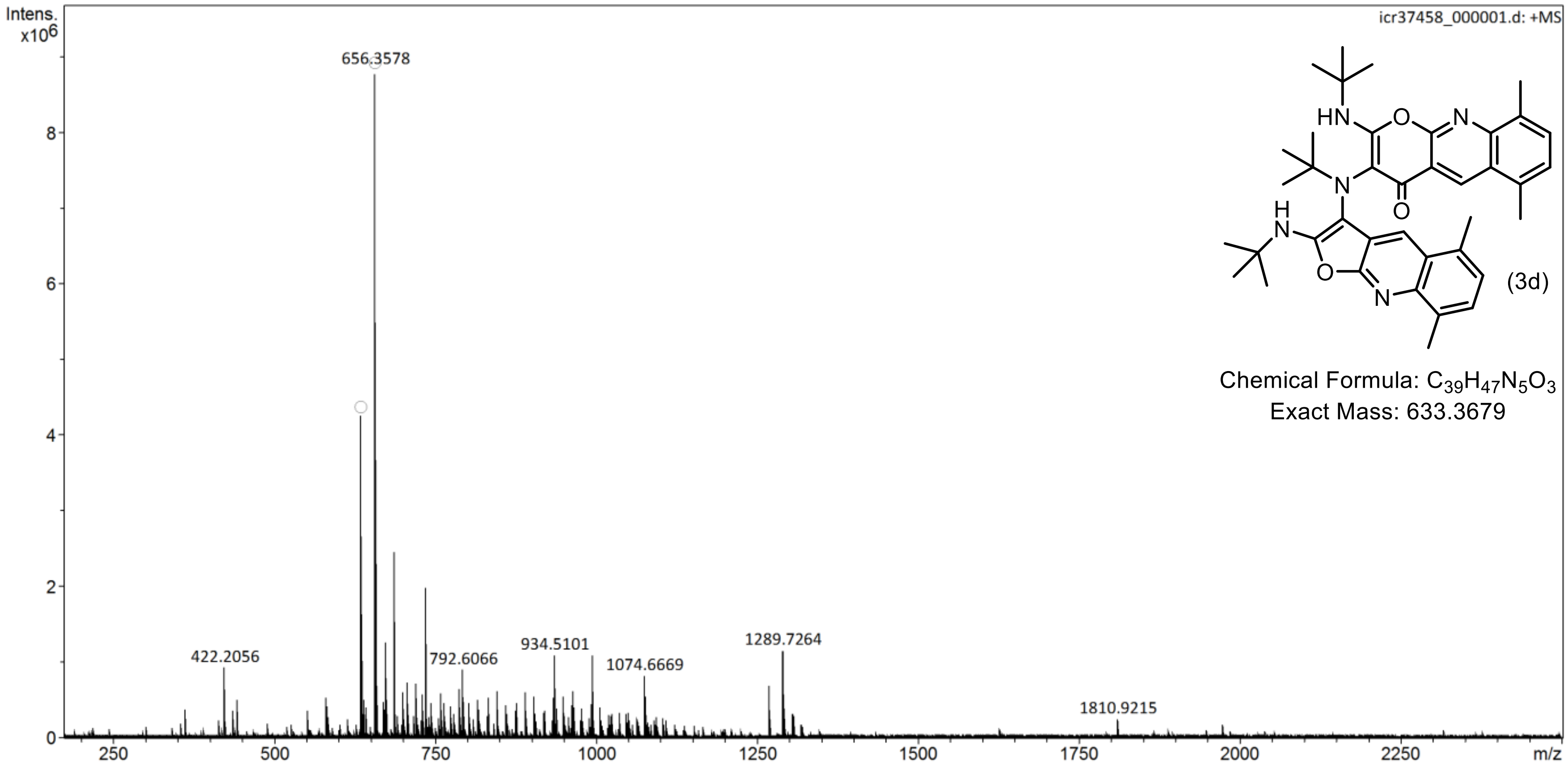


Figure S56. HRMS-ESI 3d.

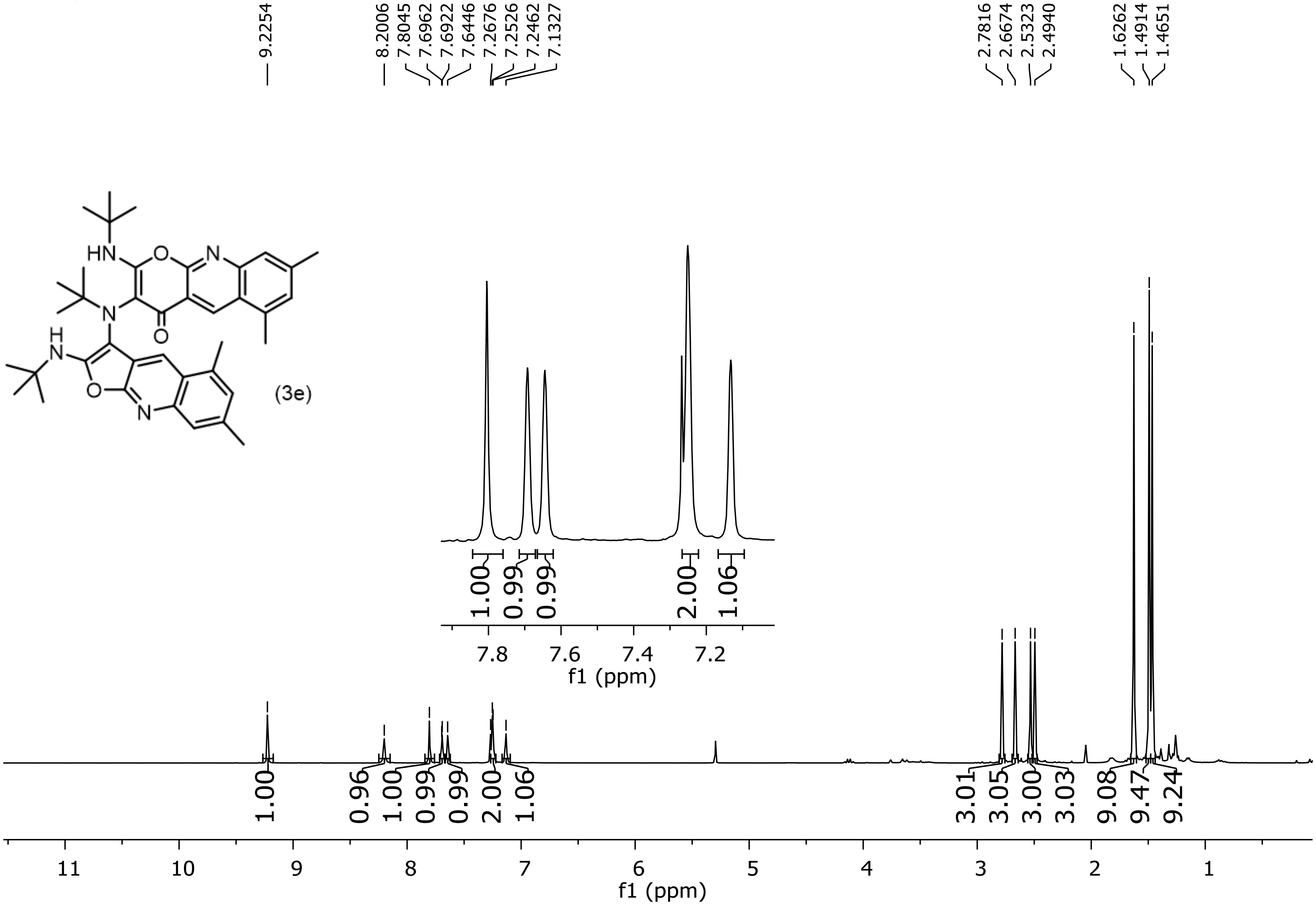


Figure S57. ¹H NMR 3e.

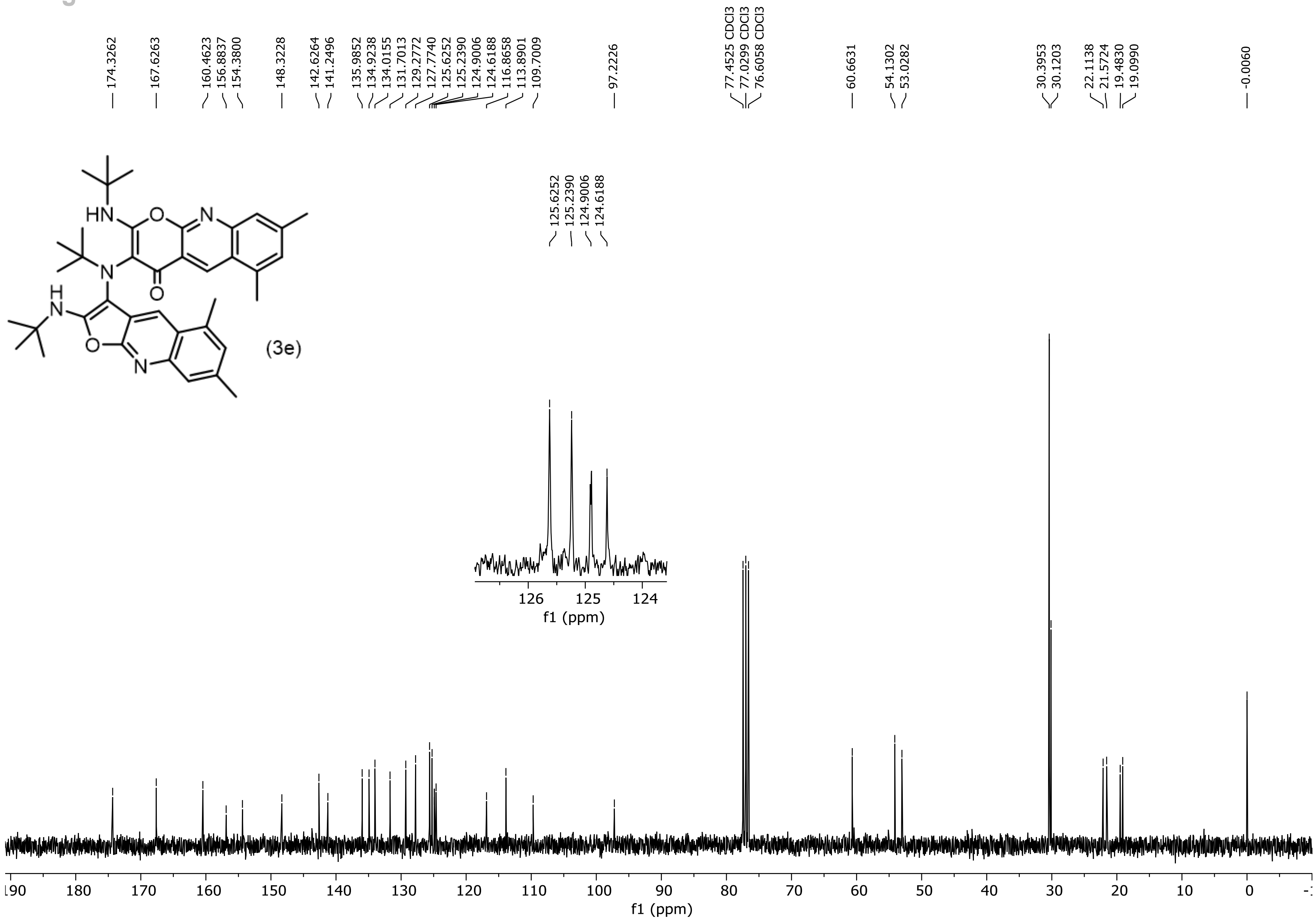


Figure S58. ^{13}C NMR 3e.

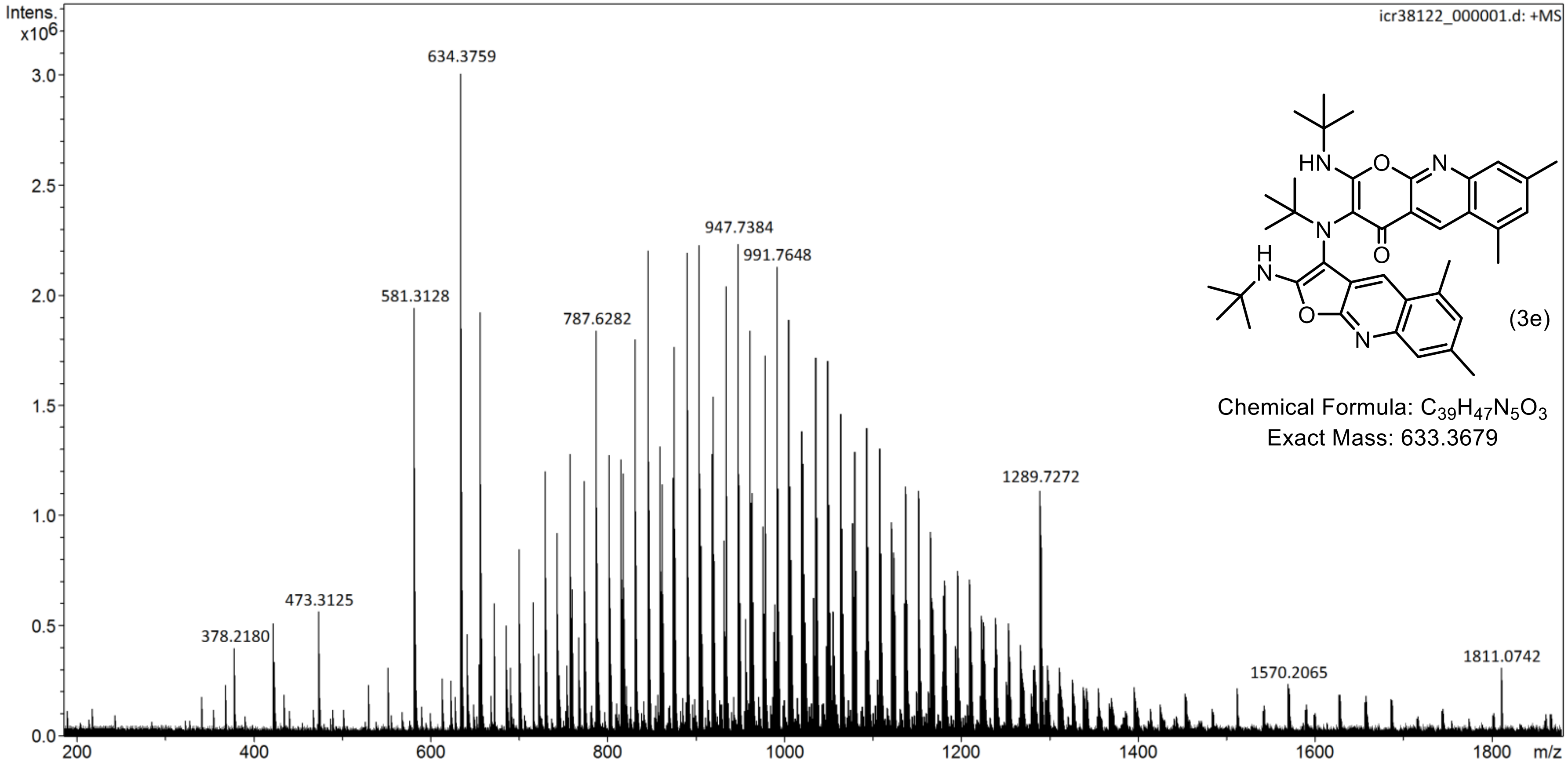


Figure S59. HRMS-ESI 3e.

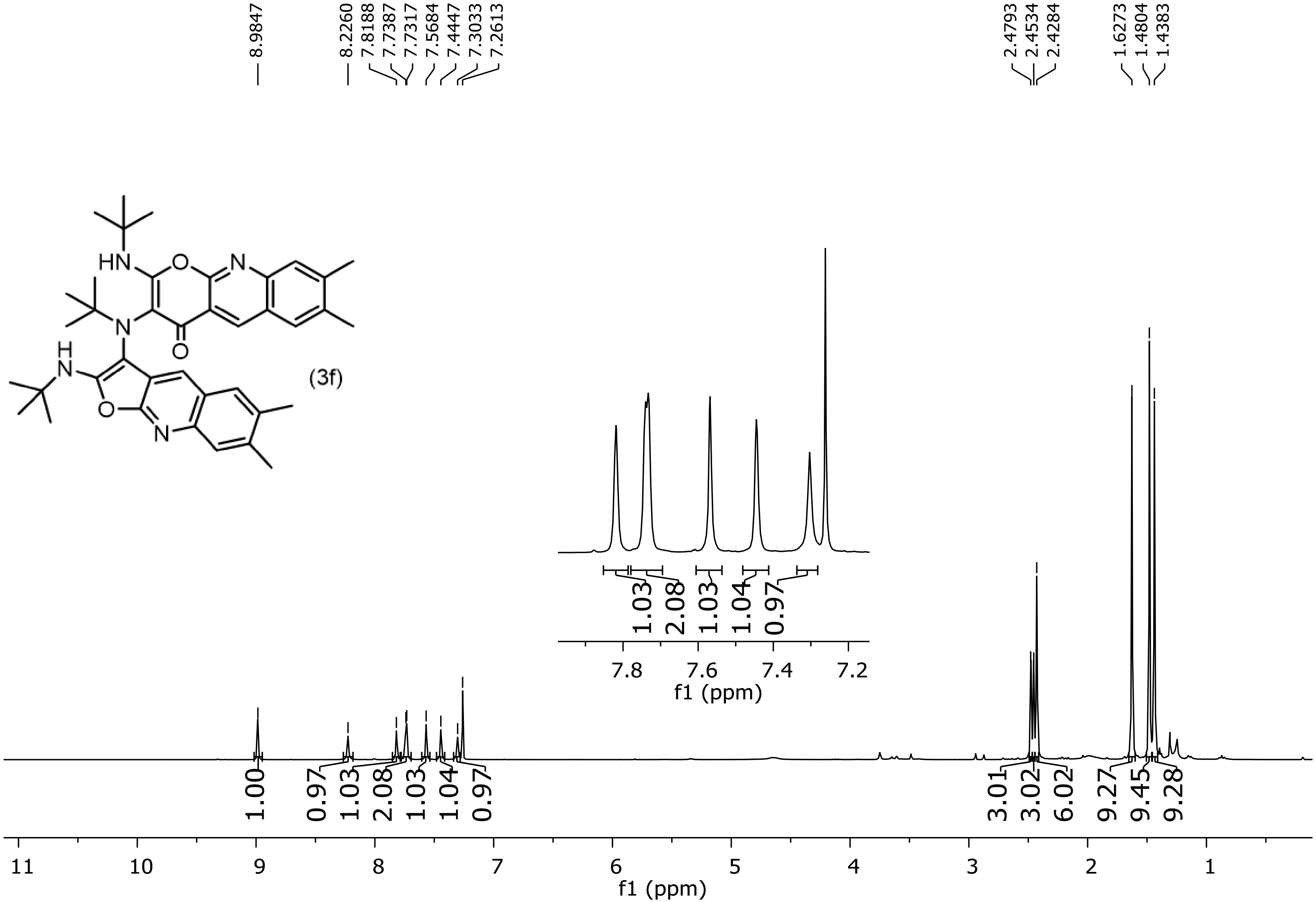


Figure S60. [1]H NMR 3f.

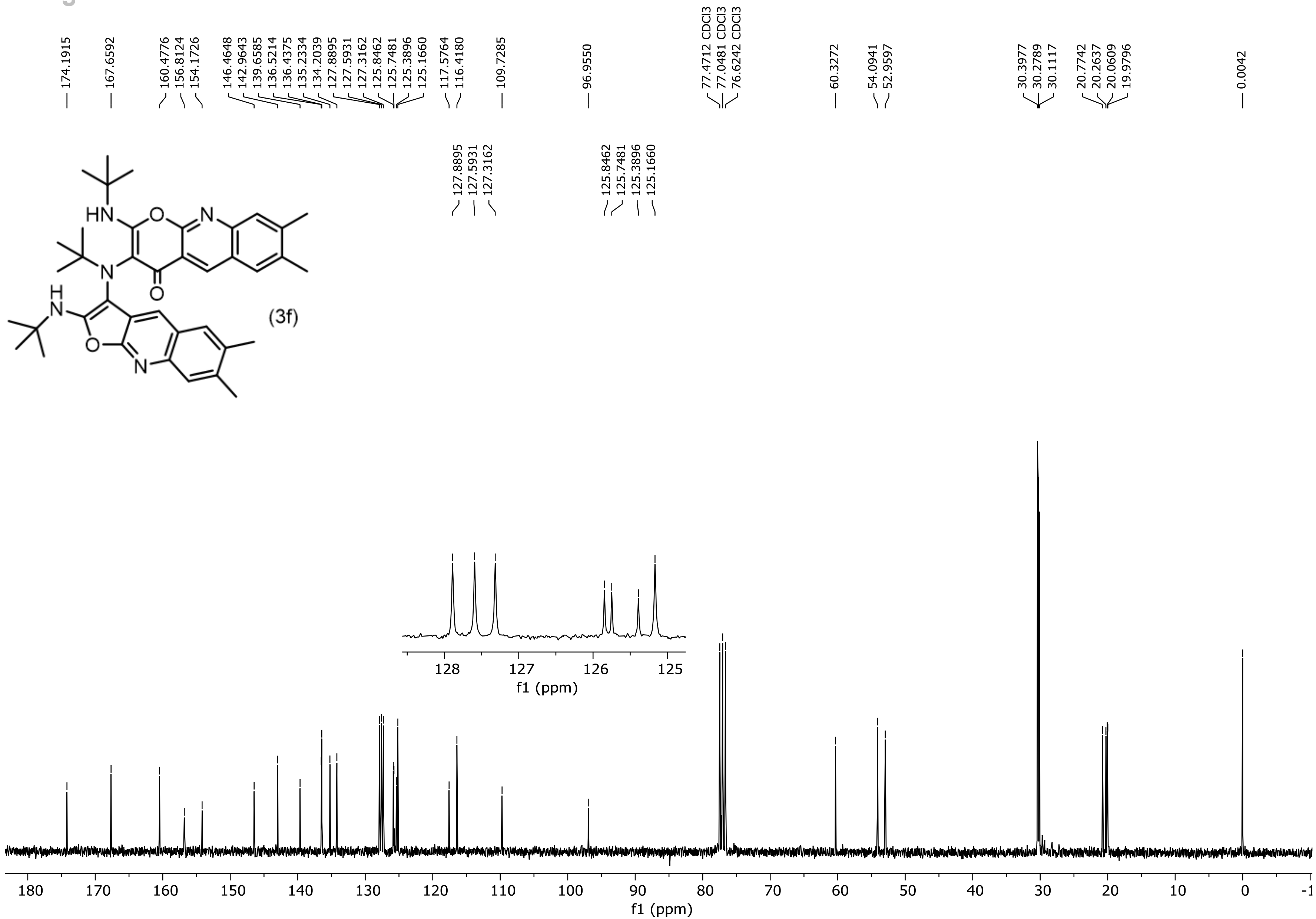


Figure S61. ^{13}C NMR 3f.

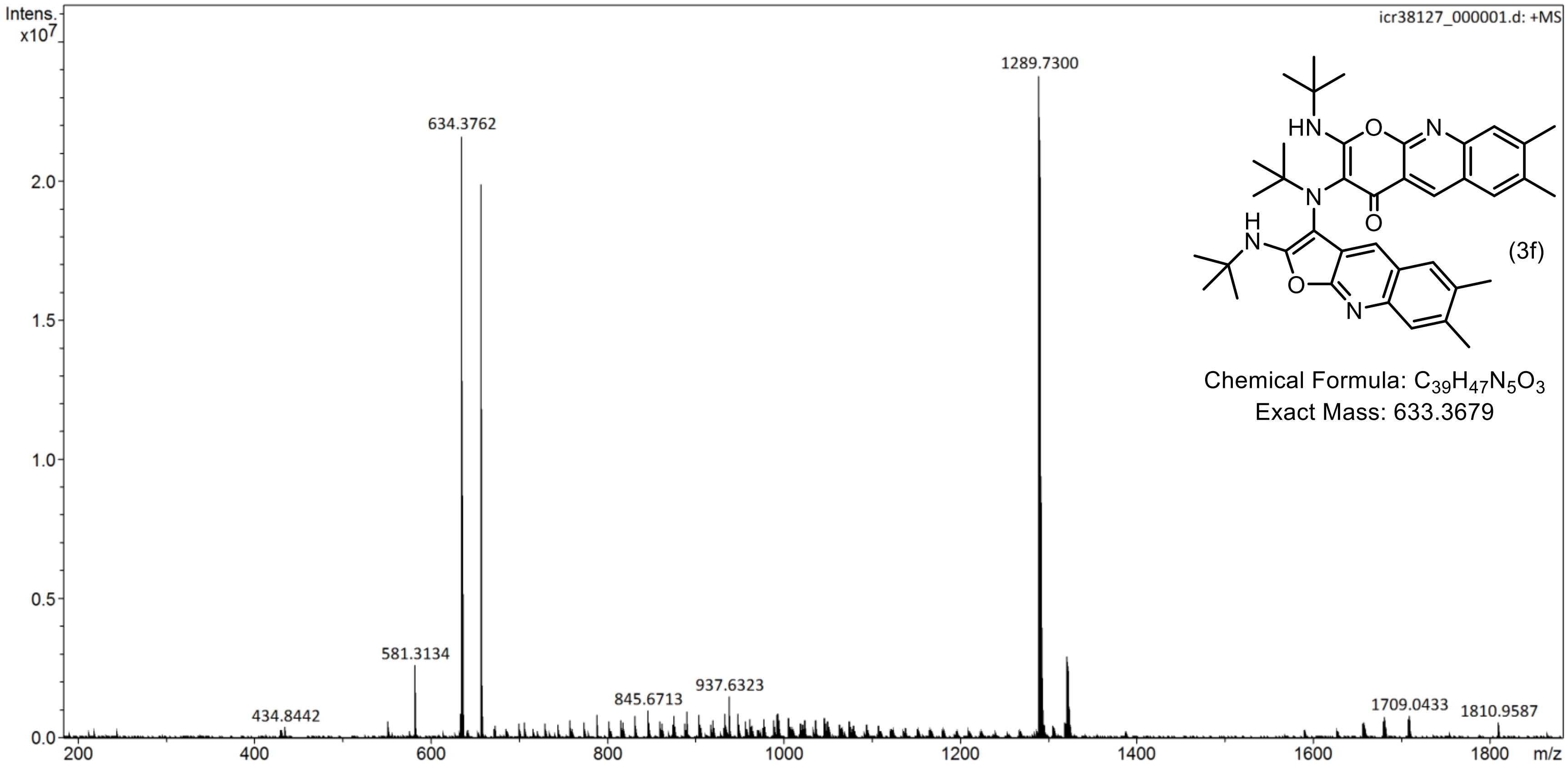
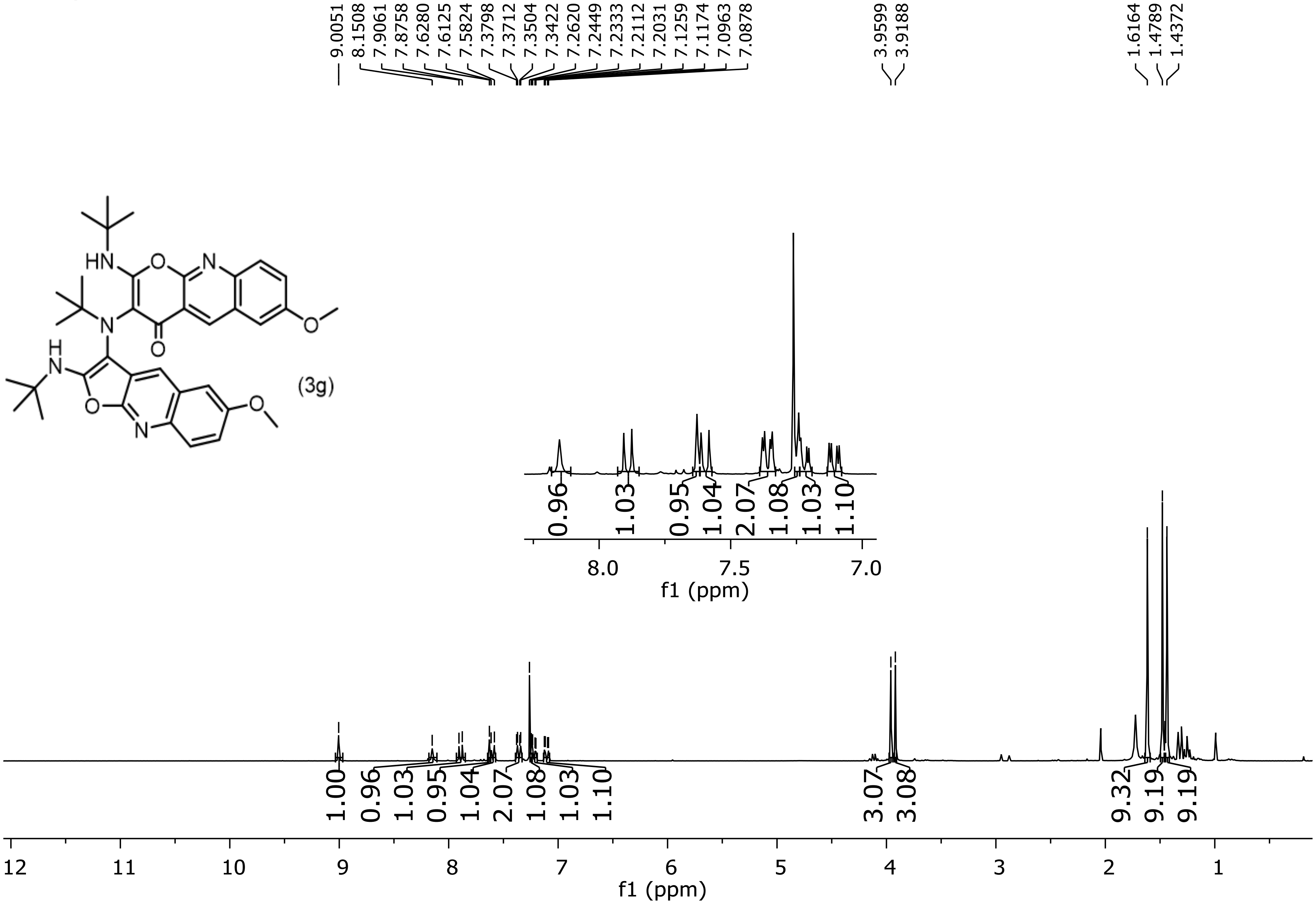


Figure S62. HRMS-ESI 3f.



(3g)

Figure S63. ^{1}H NMR 3g.

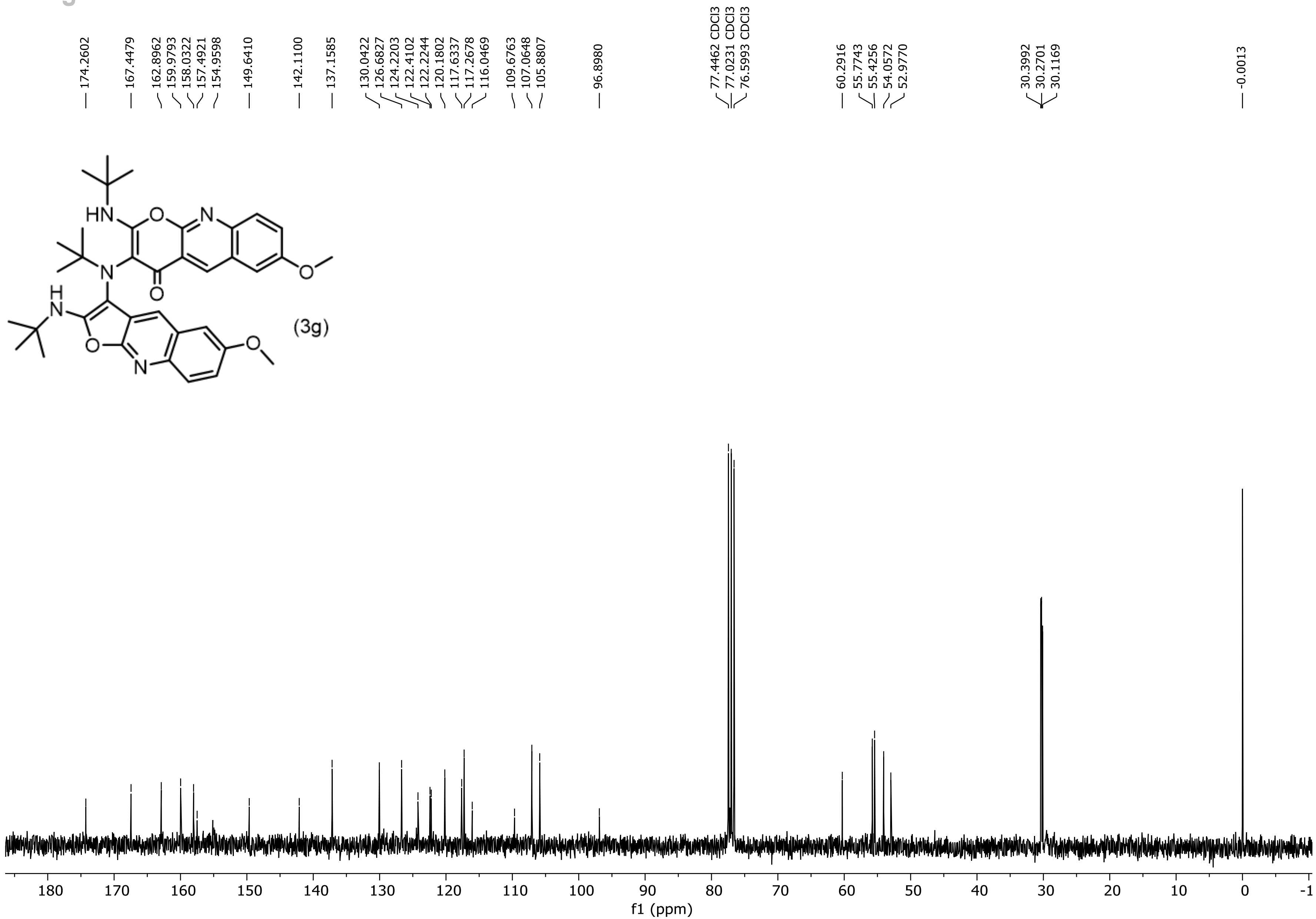


Figure S64. ^{13}C NMR 3g.

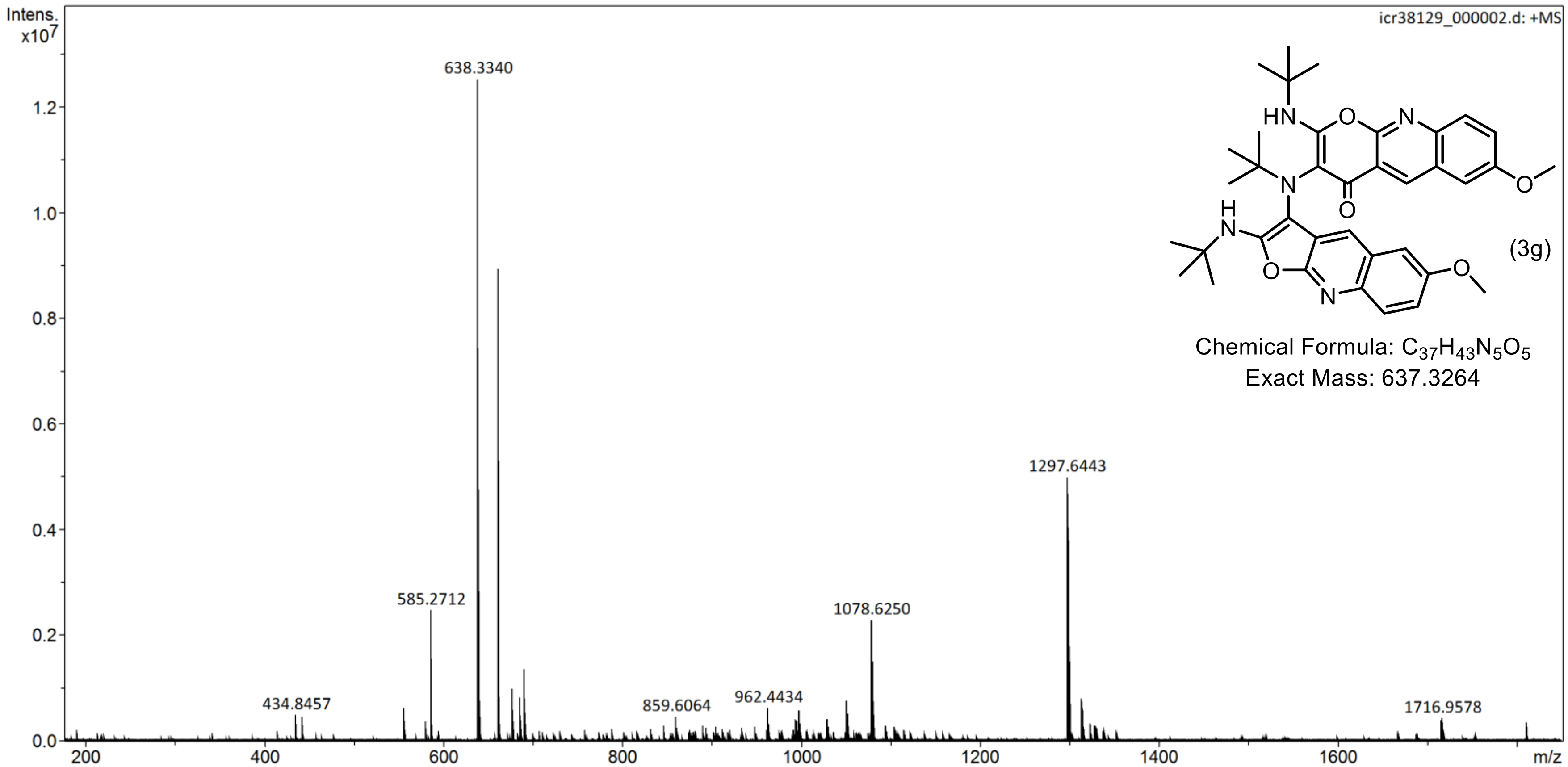


Figure S65. HRMS-ESI 3g.

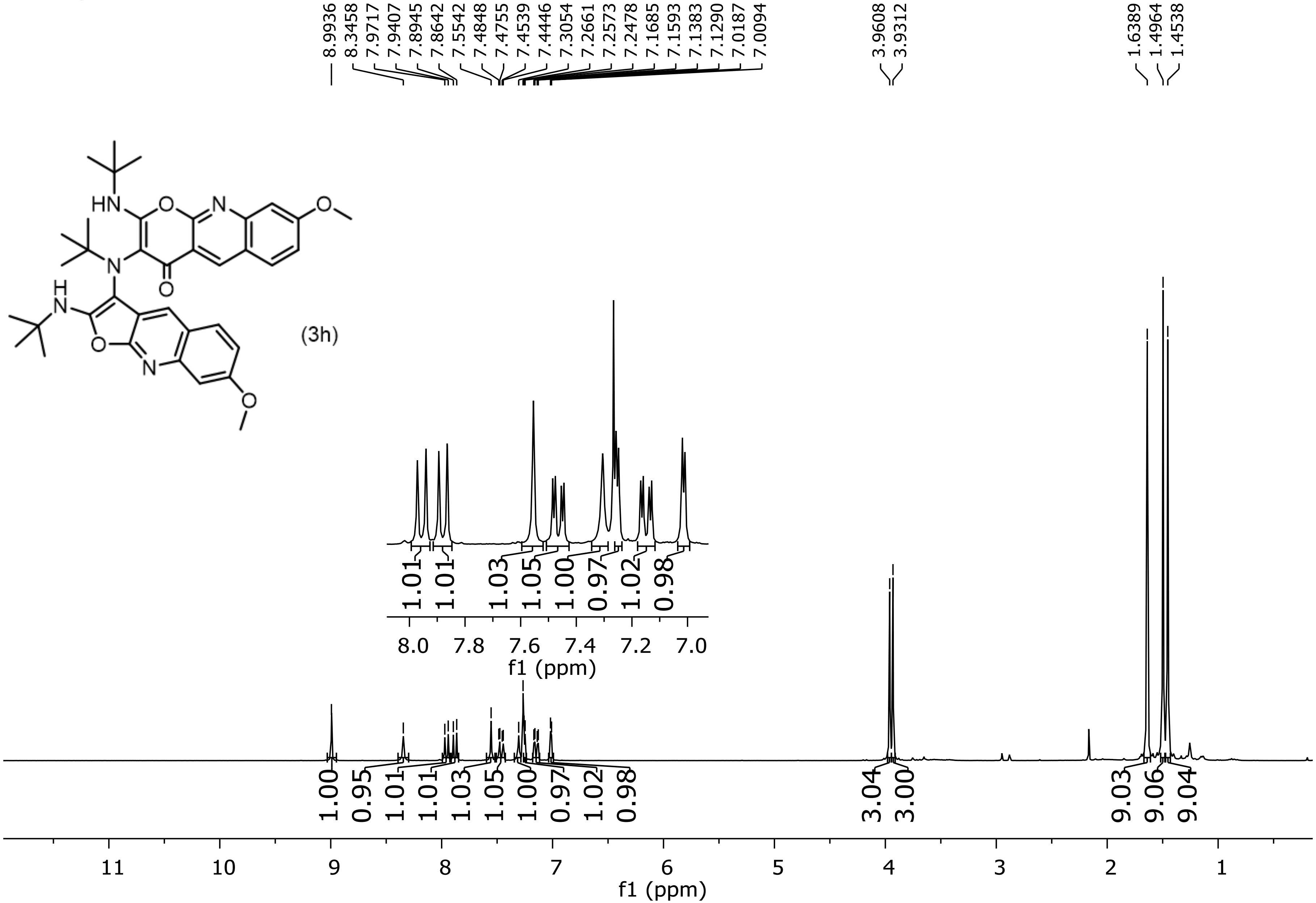


Figure S66. ^{1}H NMR 3h.

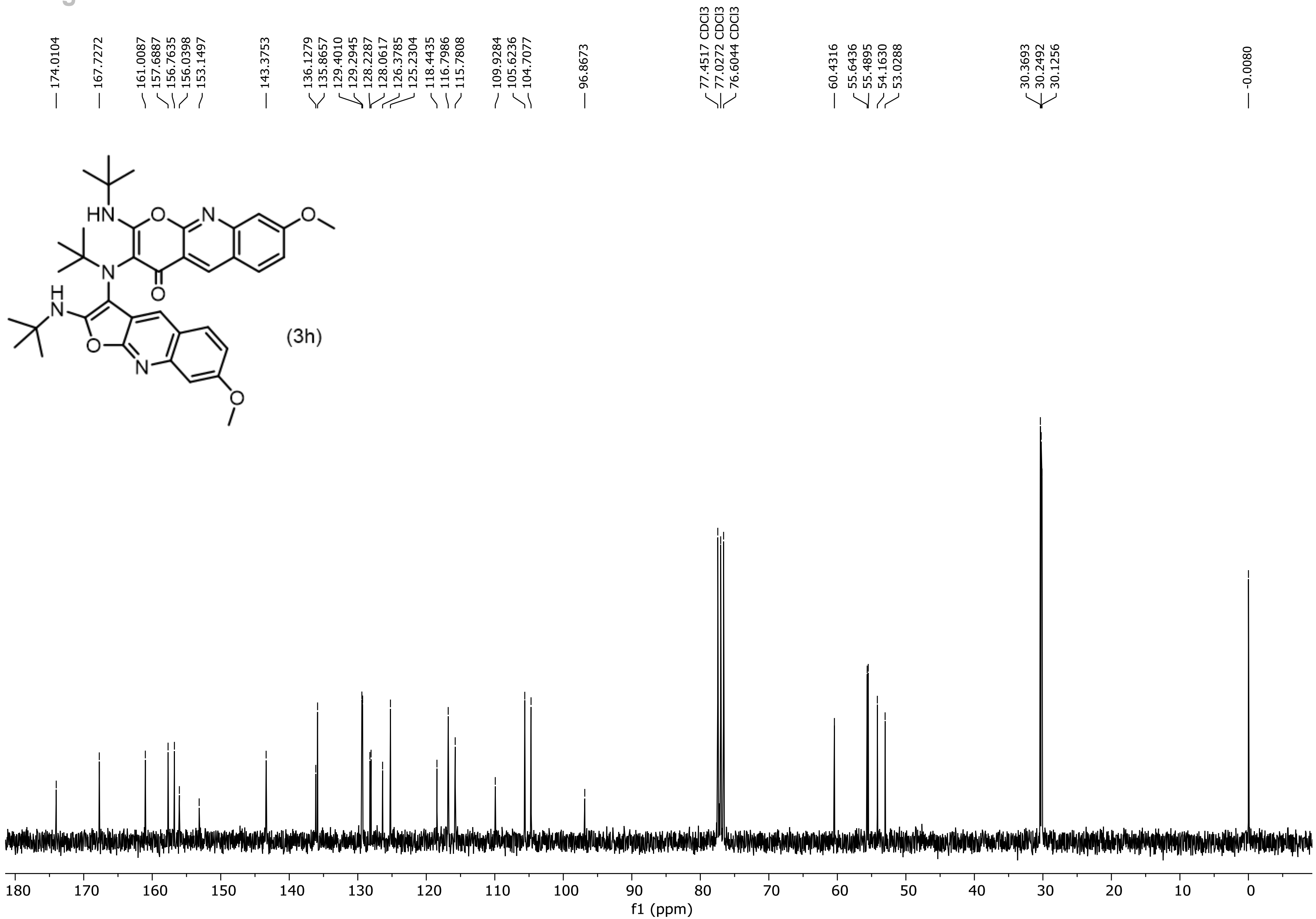


Figure S67. ^{13}C NMR 3h.

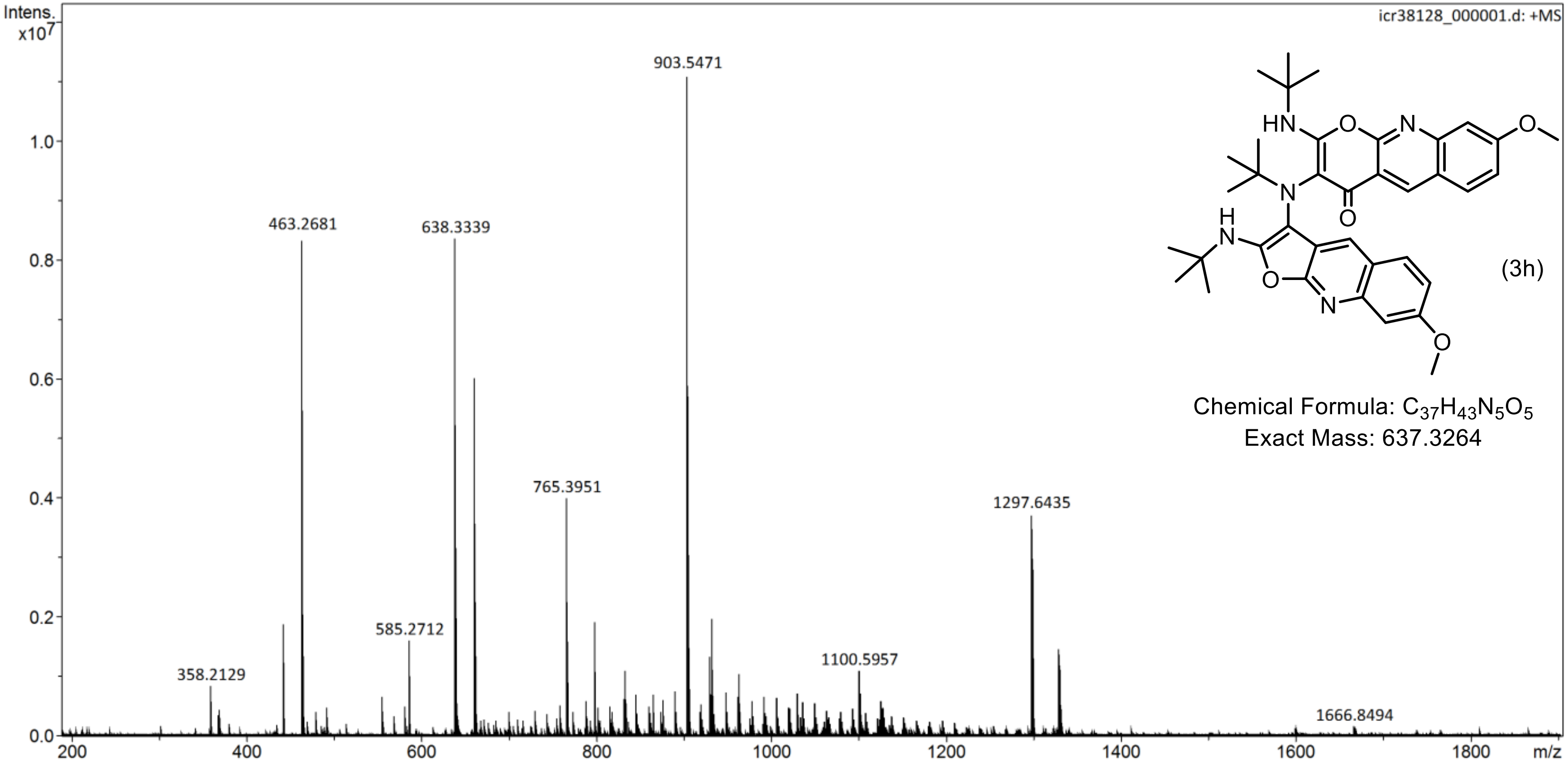
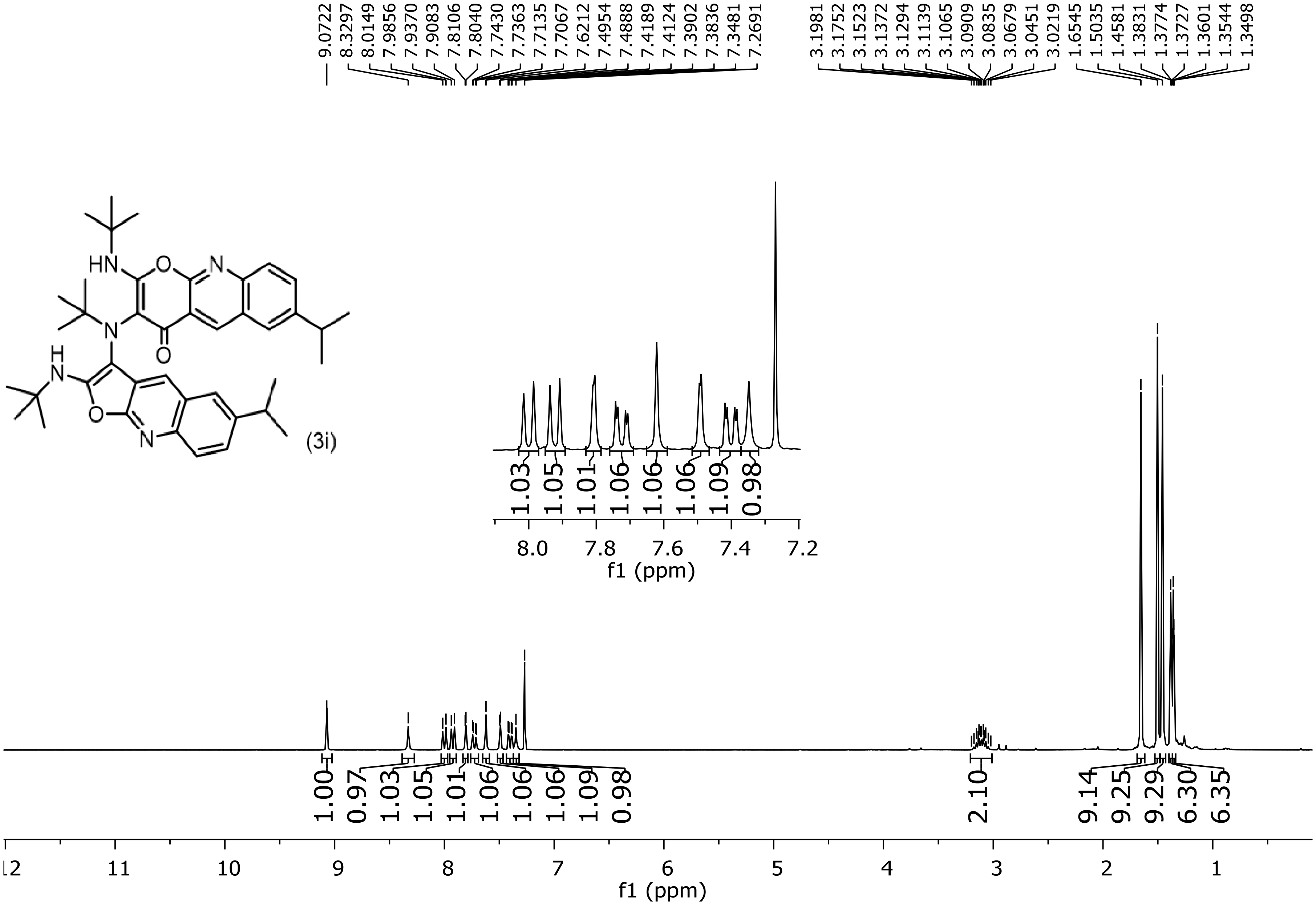
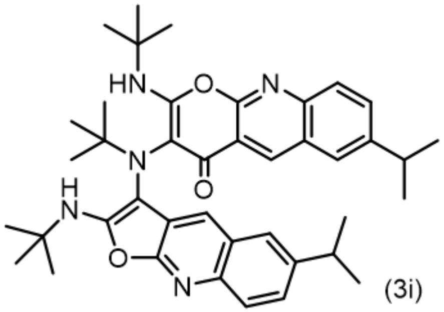


Figure S68. HRMS-ESI 3h.



(3i)

Figure S69. ^{1}H NMR 3i.



(3i)

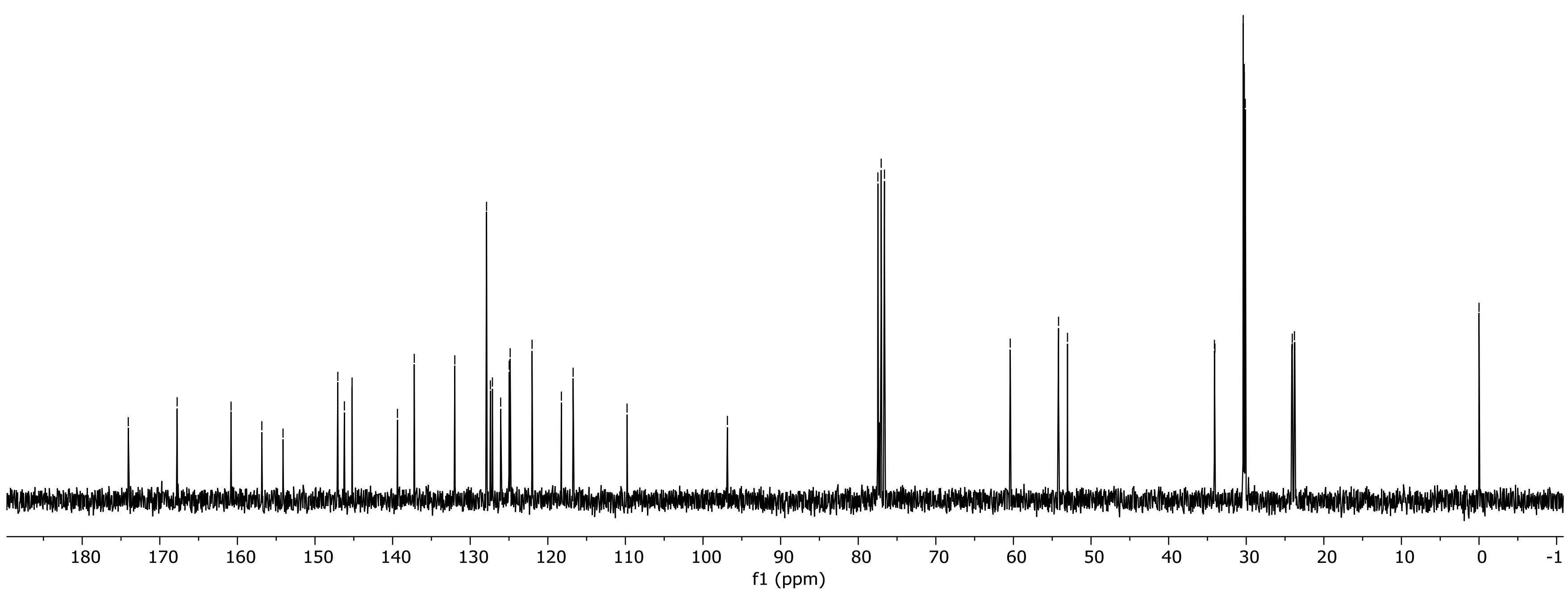
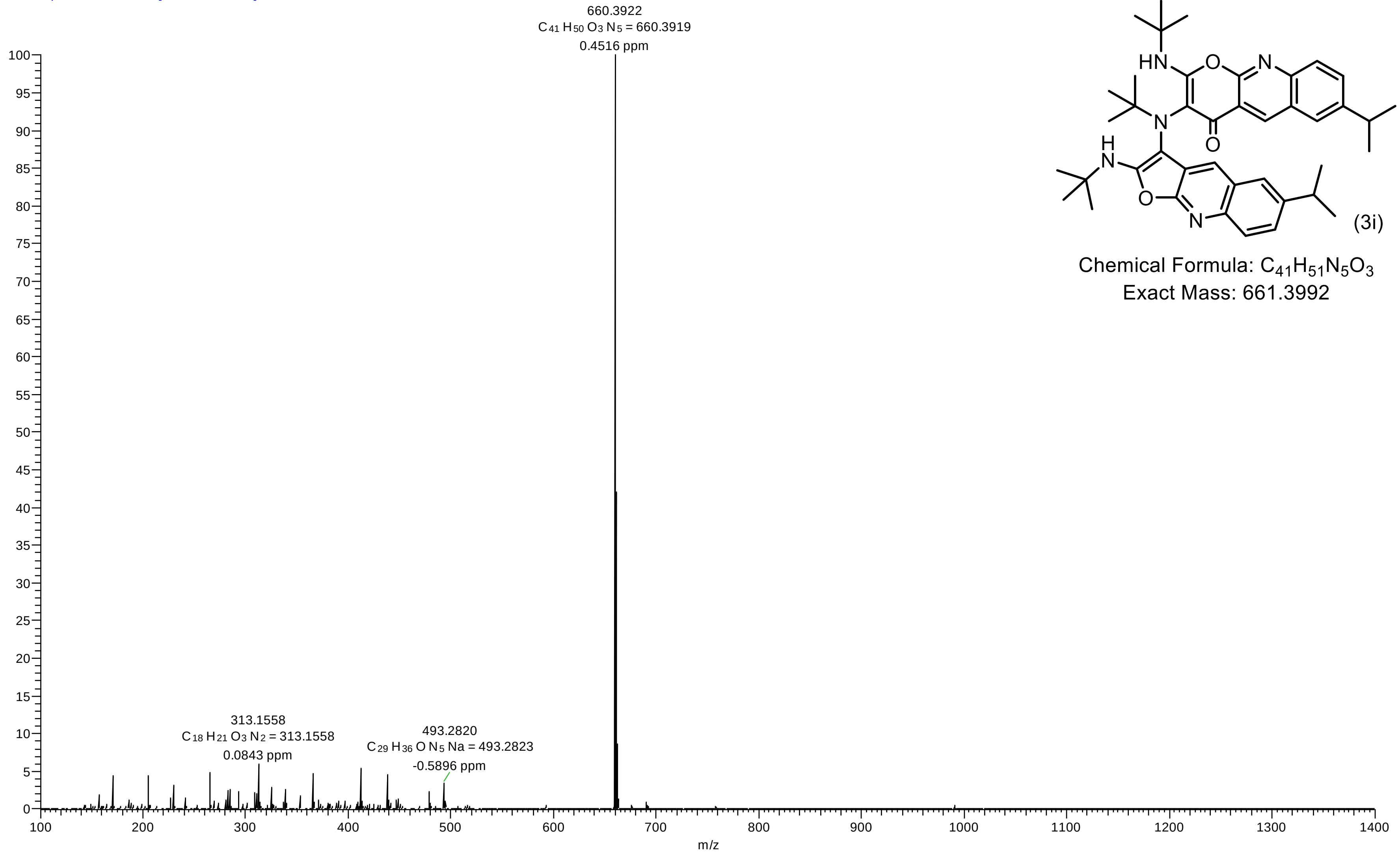


Figure S70. ^{13}C NMR 3i.

D:\data_2020\krbta72shr2 4/16/2020 10:33:23 AM

krbta72shr2 #1 RT: 0.02 AV: 1 NL: 6.86E6
T: FTMS - p ESI Full lock ms [100.00-1400.00]



(3i)

Chemical Formula: $C_{41}H_{51}N_5O_3$
Exact Mass: 661.3992

Figure S71. HRMS-ESI 3i.

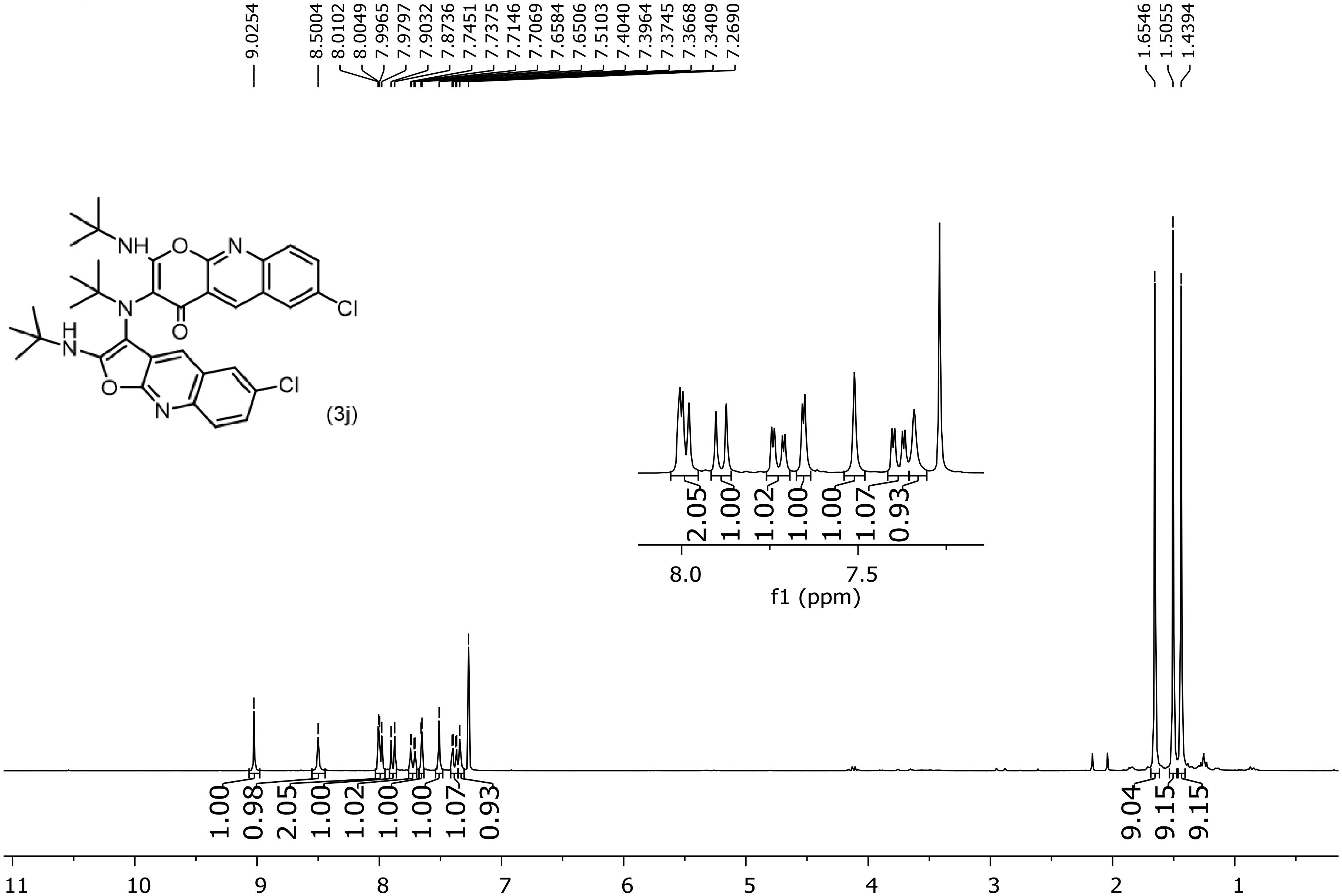
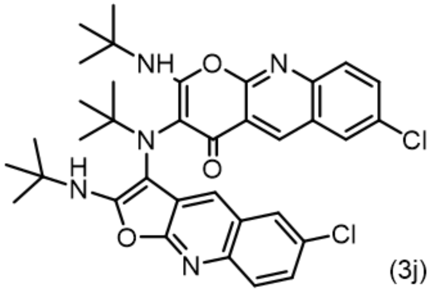


Figure S72. [1]H NMR 3j.


(3j)

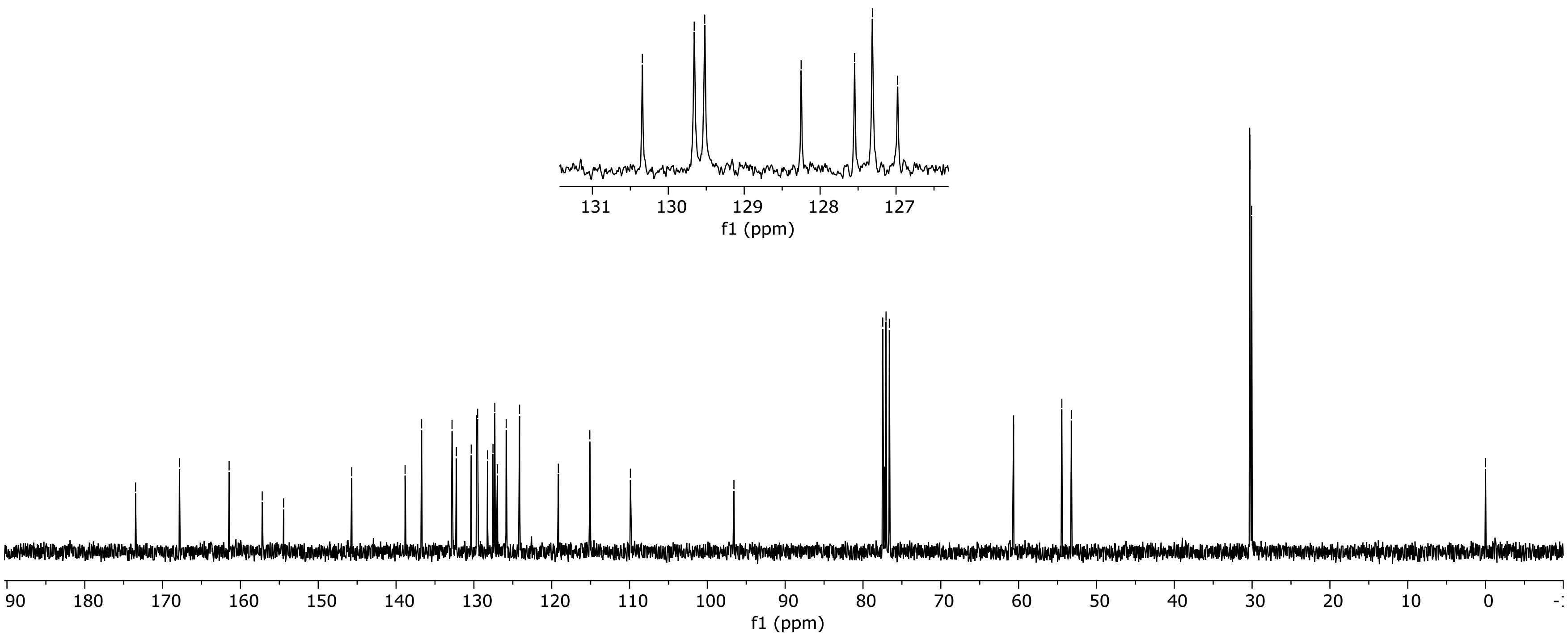


Figure S73. ^{13}C NMR 3j.

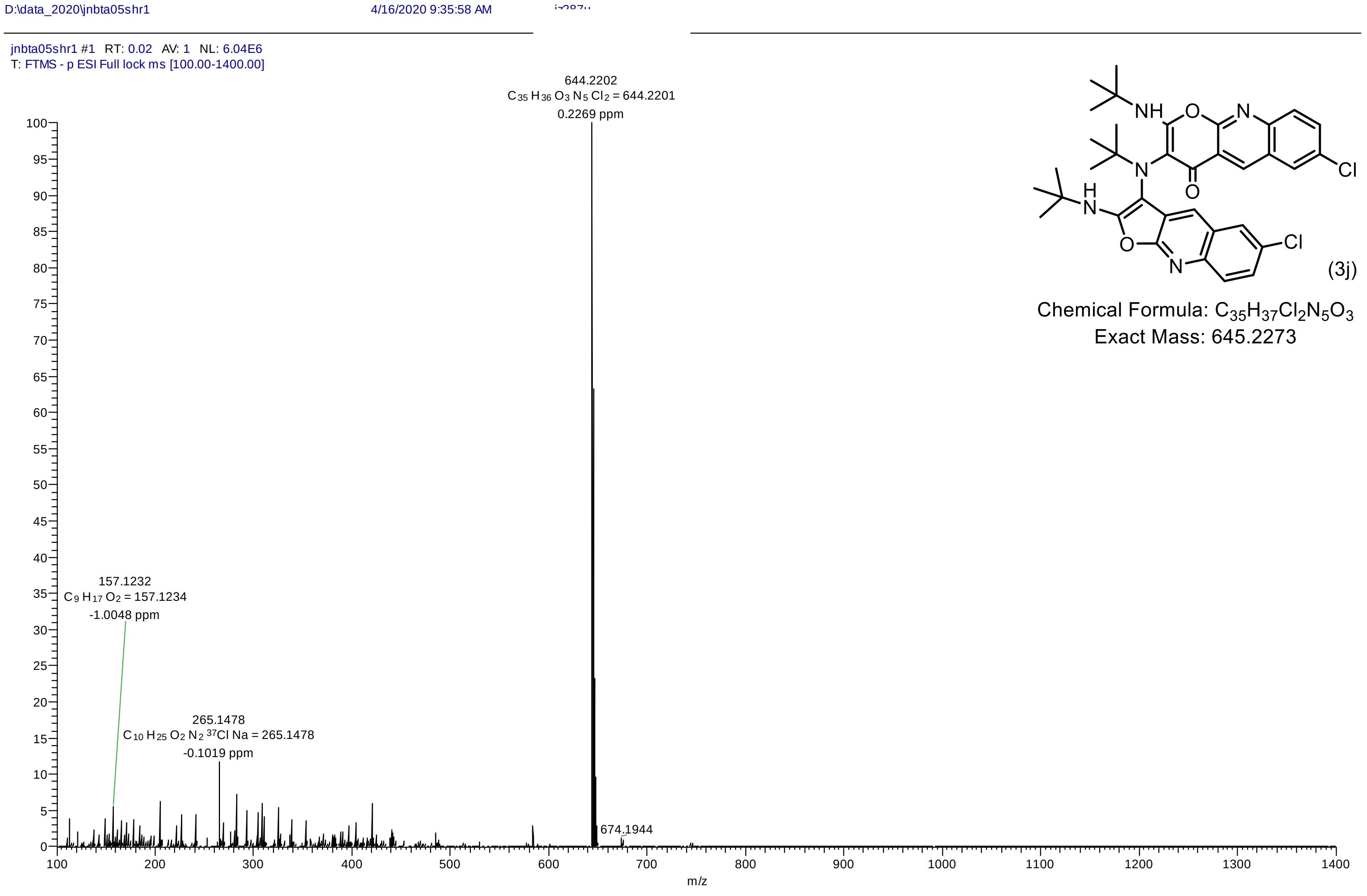


Figure S74. HRMS-ESI 3j.

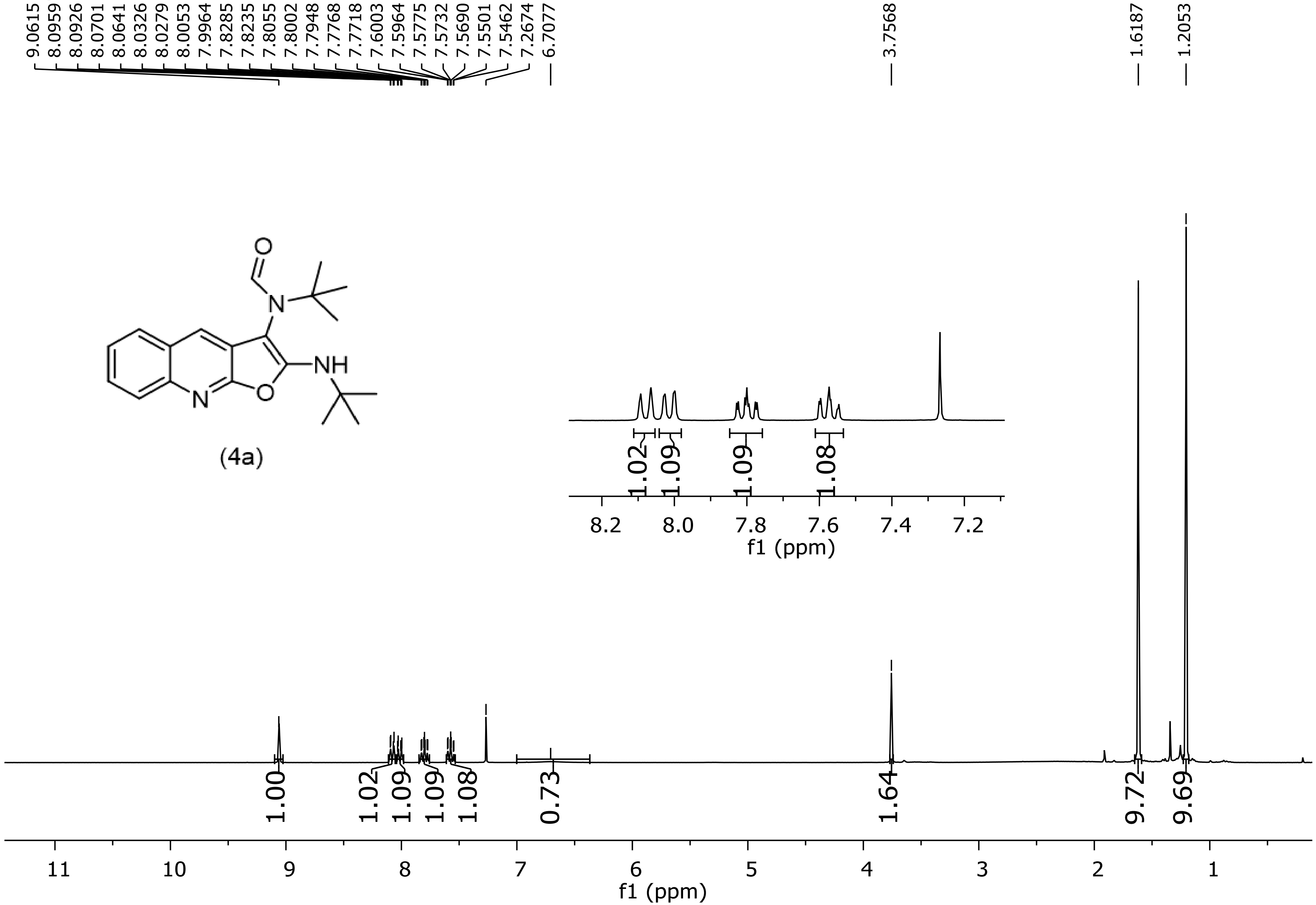


Figure S75. ^{1}H NMR 4a.

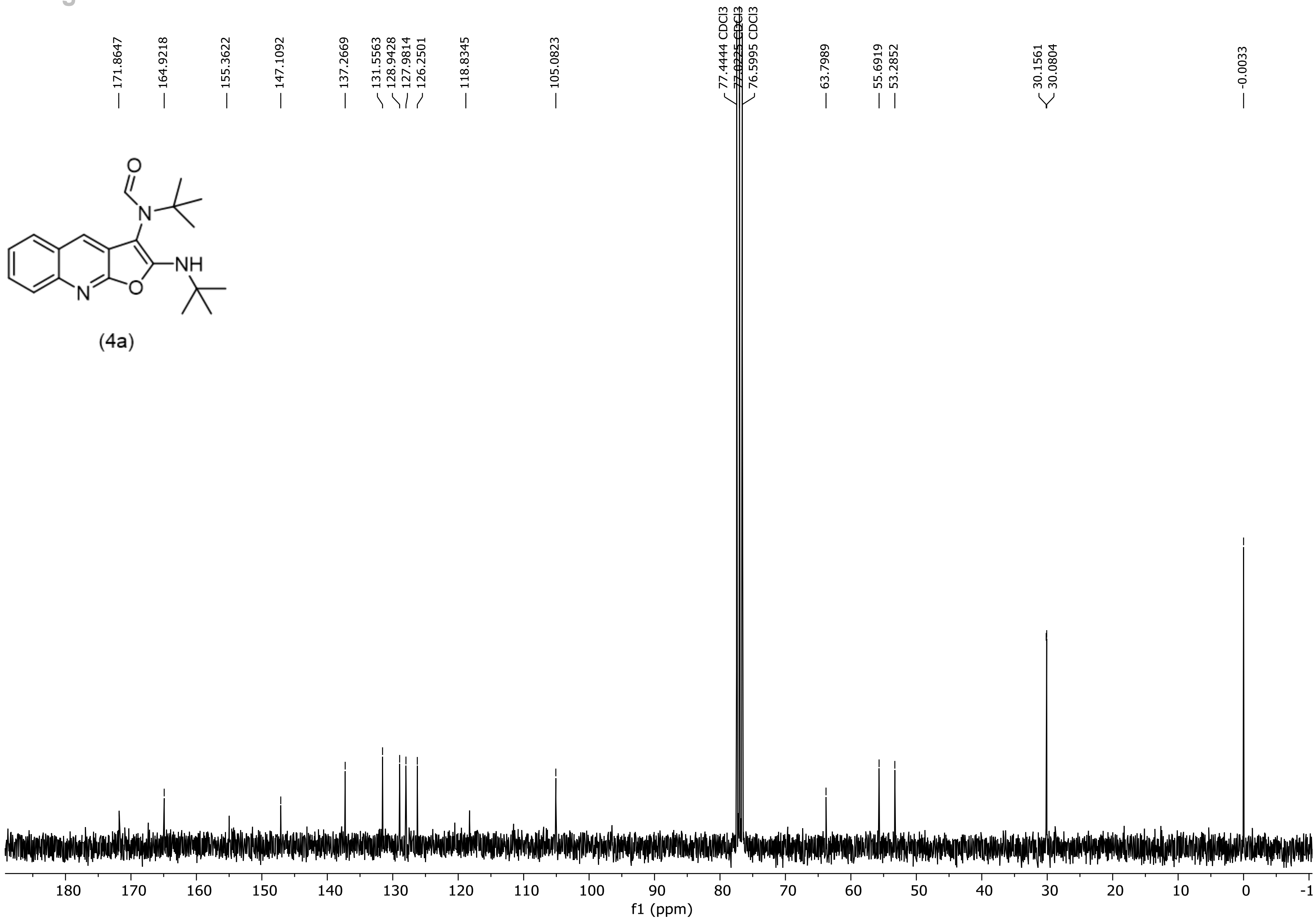


Figure S76. ^{13}C NMR 4a.

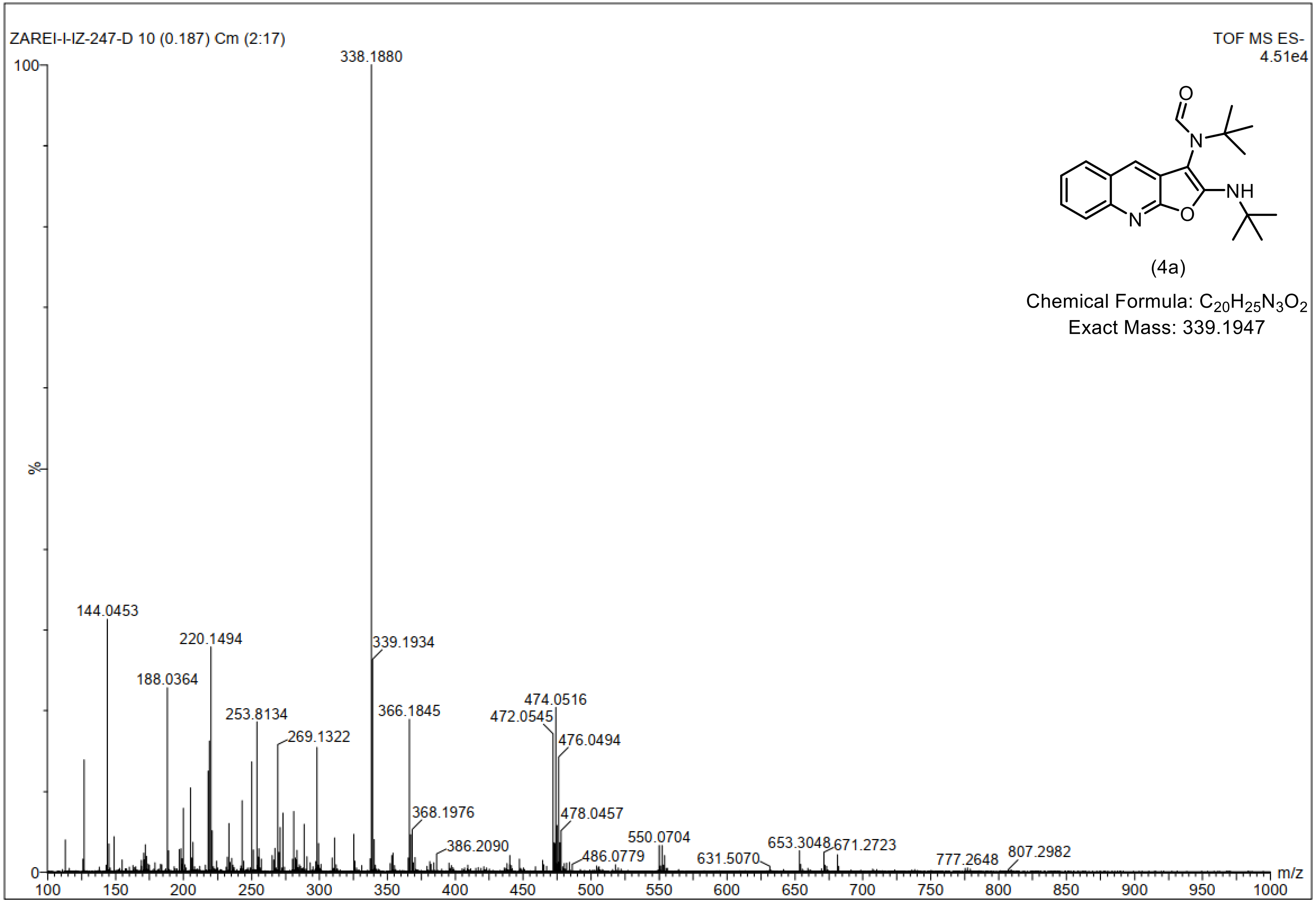


Figure S77. HRMS-ESI 4a.

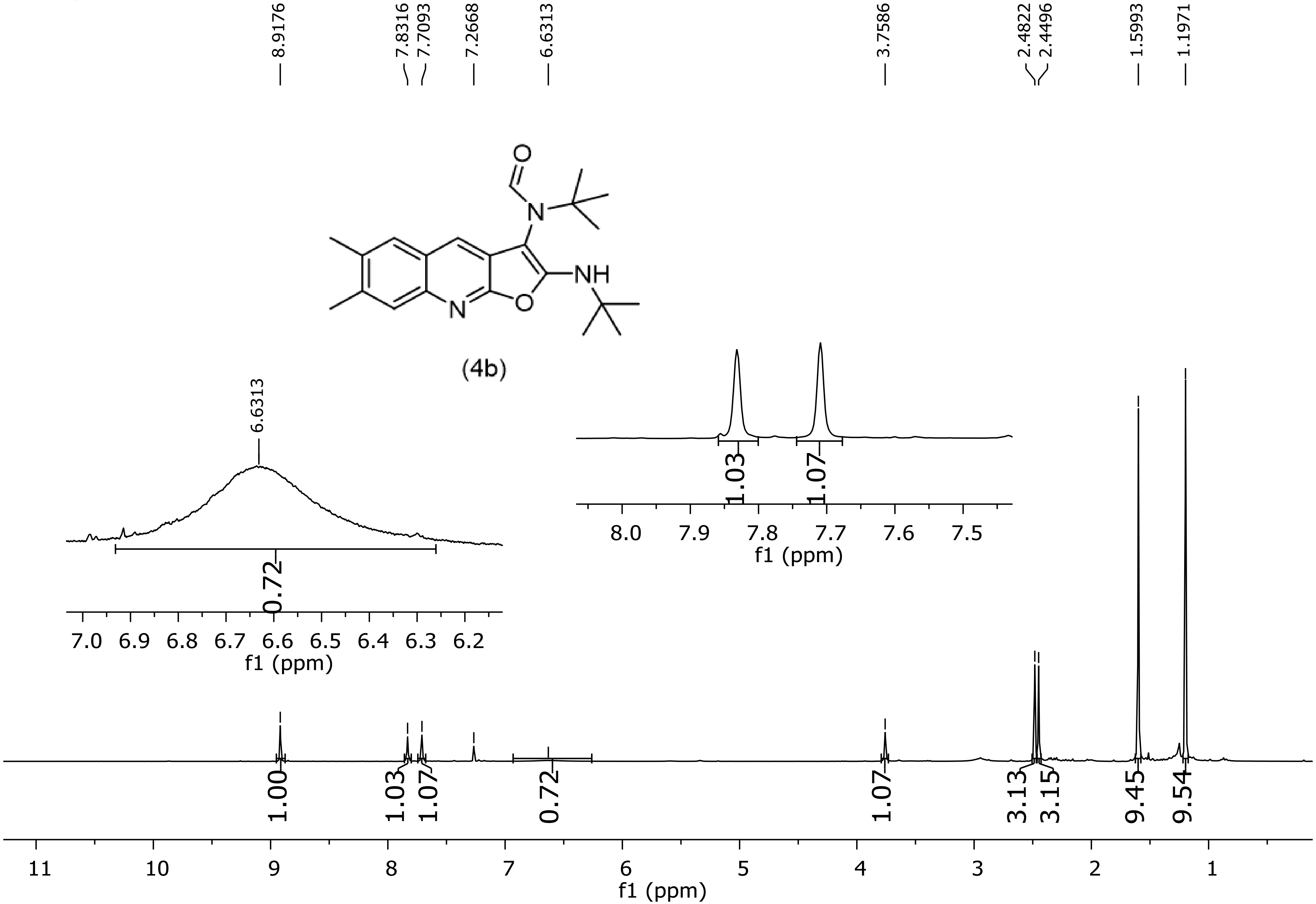
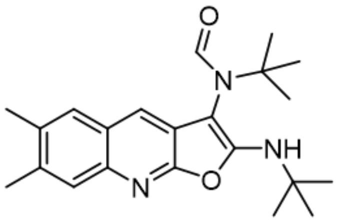


Figure S78. ^{1}H NMR 4b.



(4b)

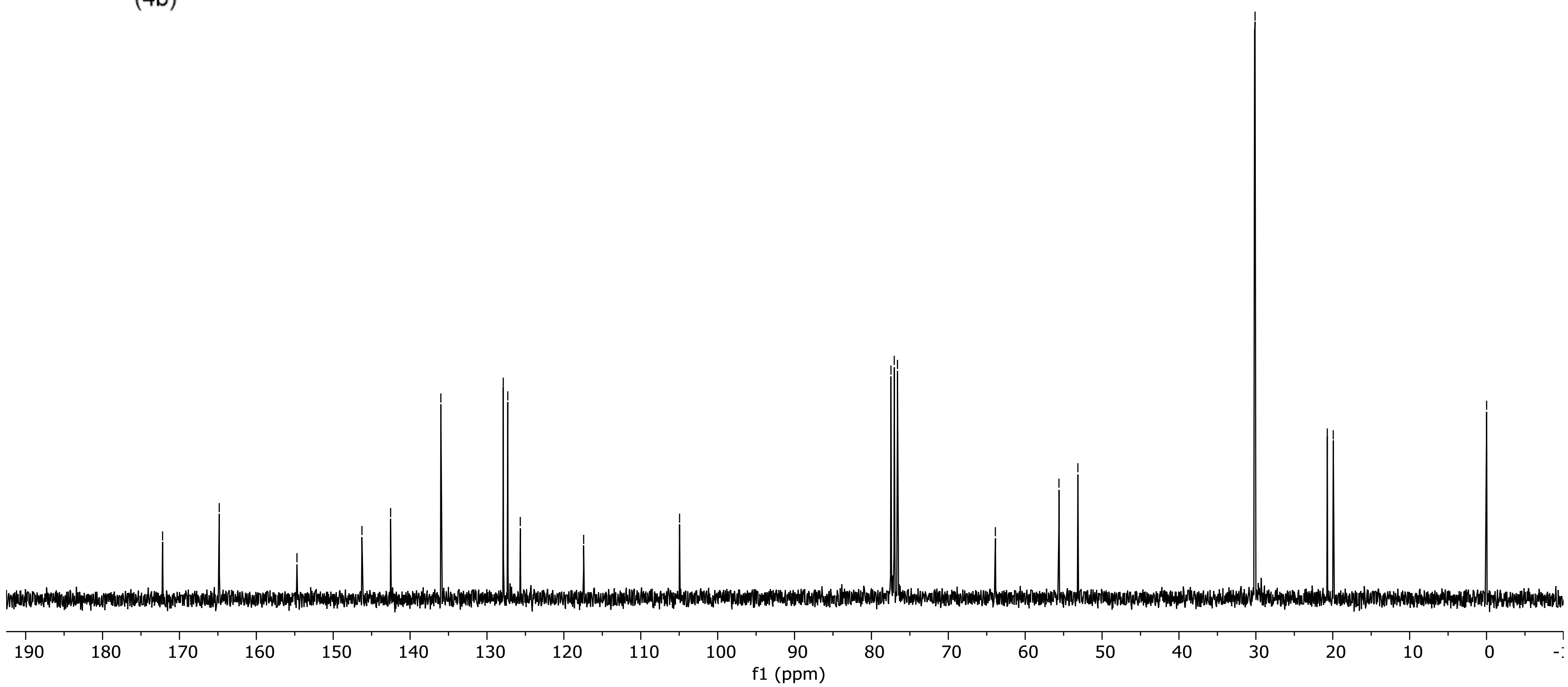

172.1944
164.8234
154.7163
146.2628
142.5308
136.0005
127.8808
127.2946
125.6708
117.4276
104.9543
77.4581 CDCl3
77.0335 CDCl3
76.6108 CDCl3
63.8806
55.6106
53.1486
30.1662
30.1073
20.7083
19.9346
-0.0162
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Figure S79. ^{13}C NMR 4b.

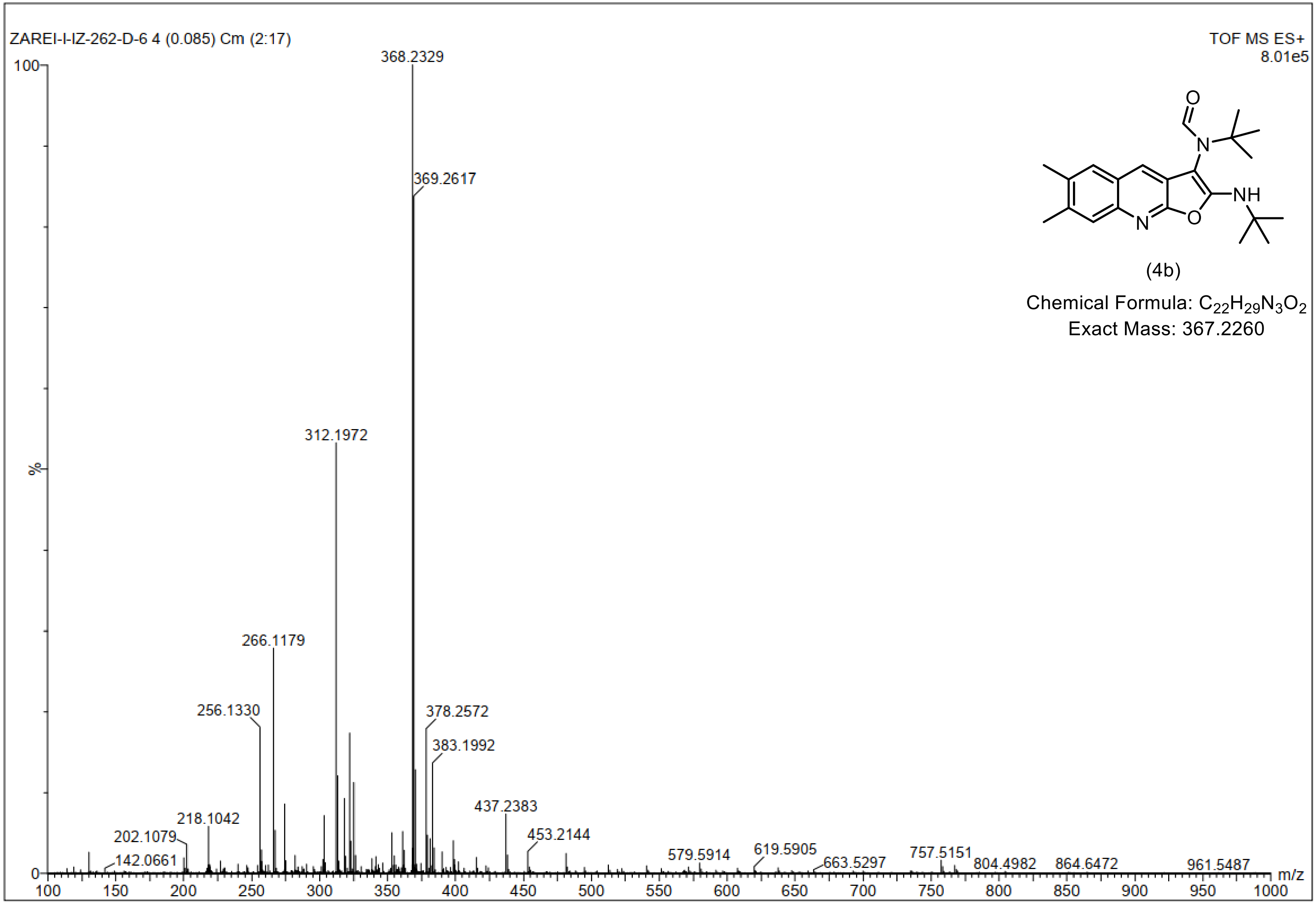


Figure S80. HRMS-ESI 4b.

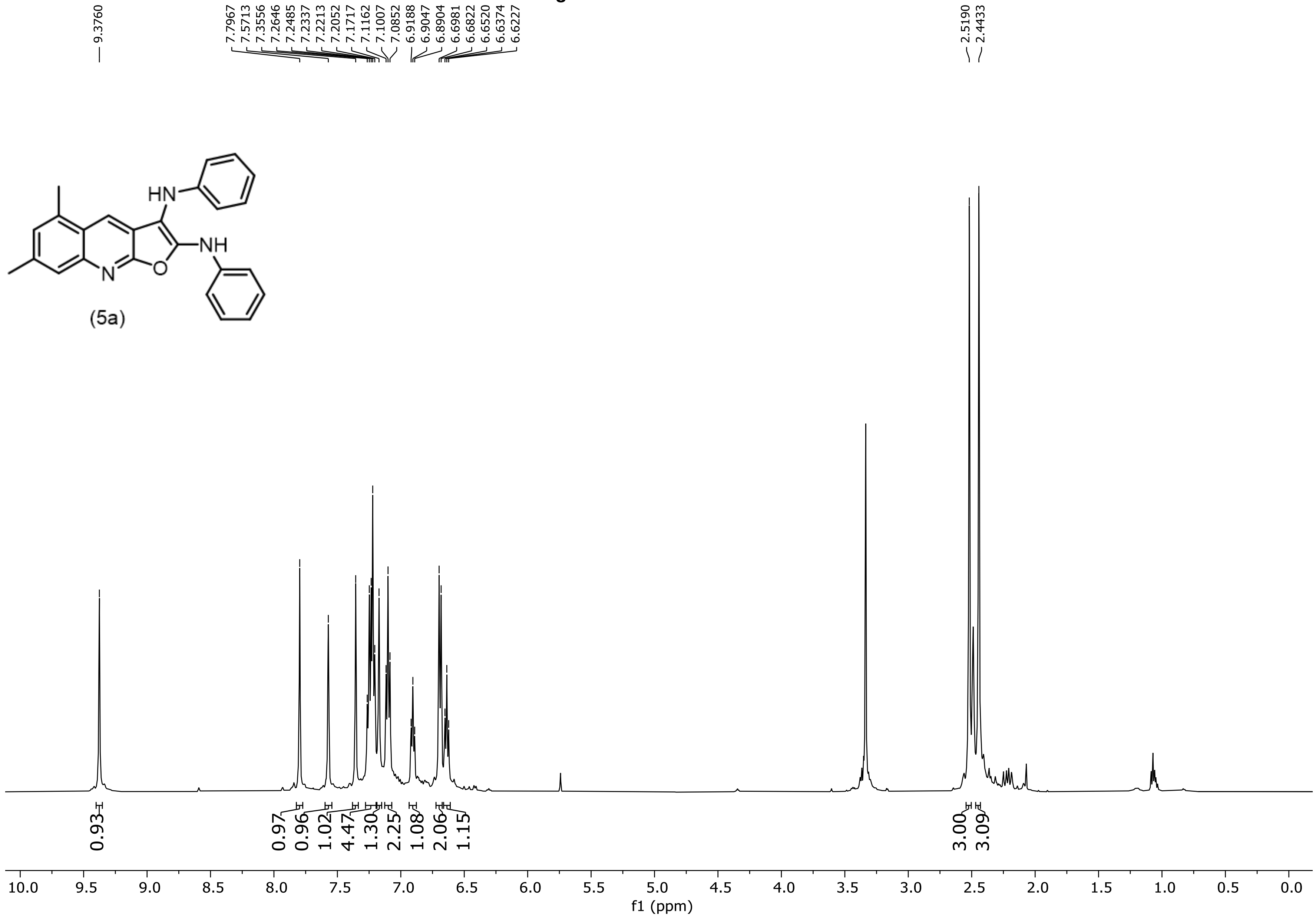


Figure S81. ^{1}H NMR 5a.

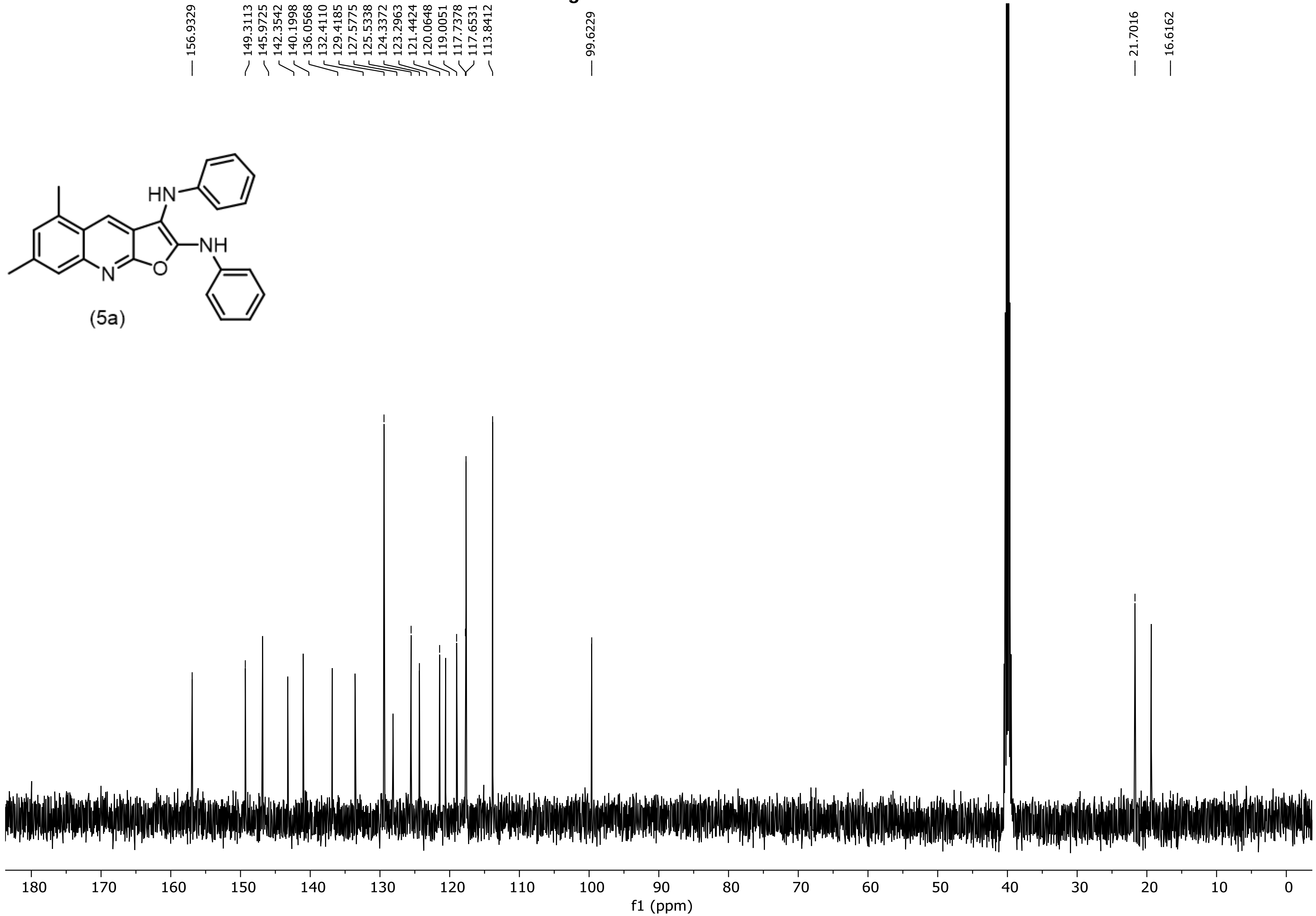


Figure S82. ^{13}C NMR 5a.

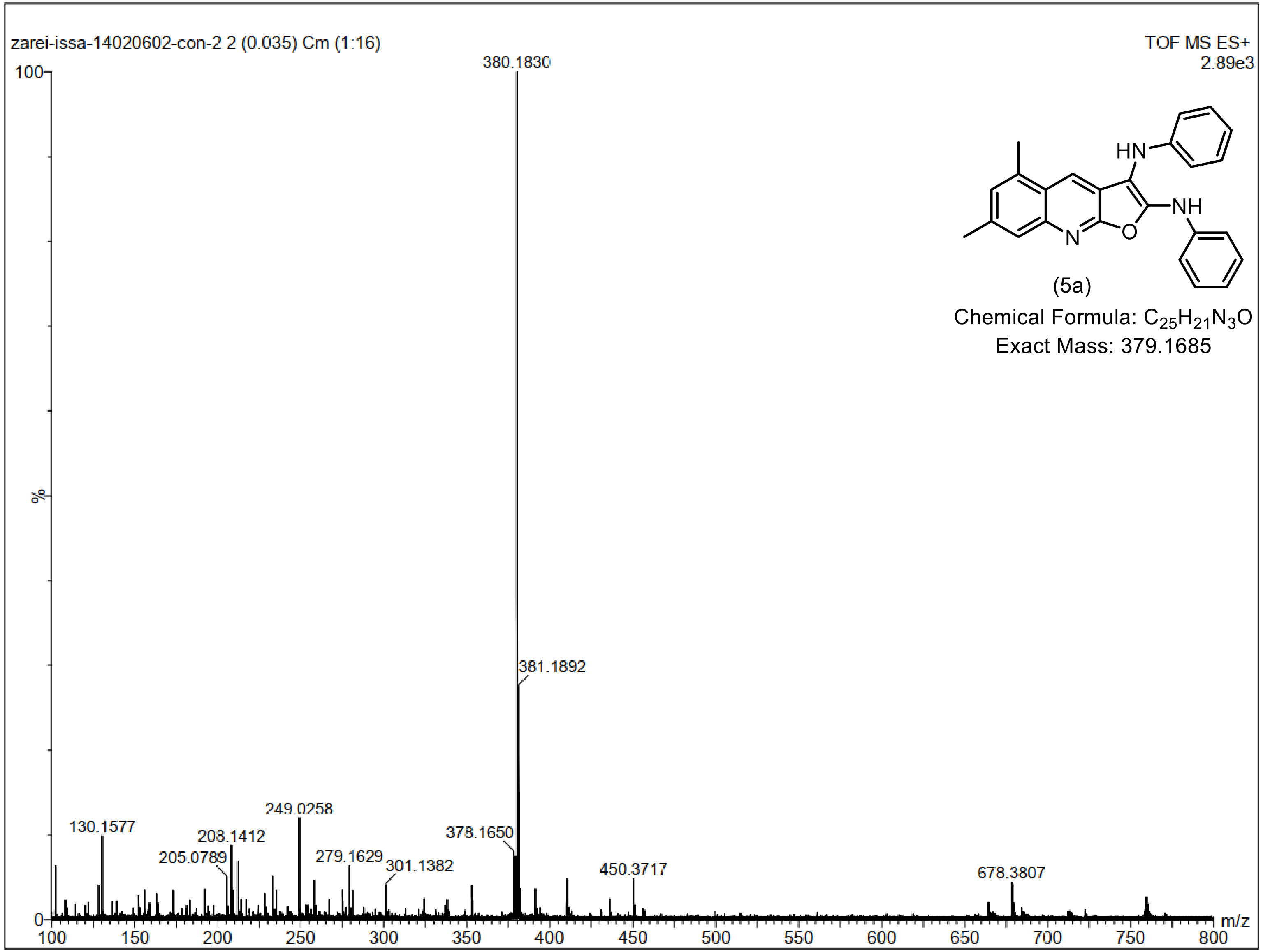
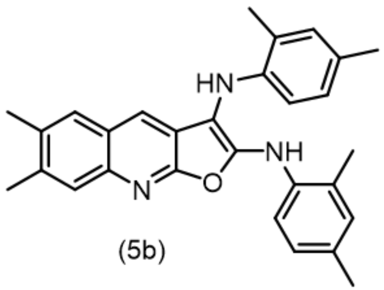


Figure S83. HRMS-ESI 5a.



(5b)

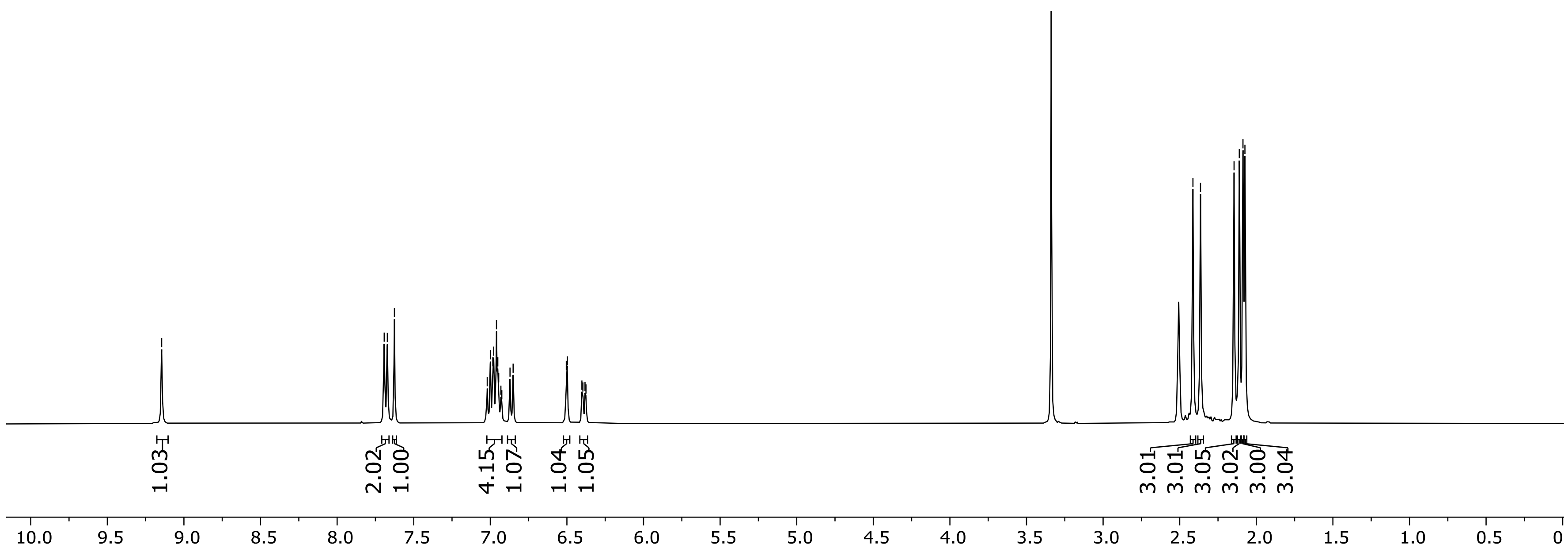
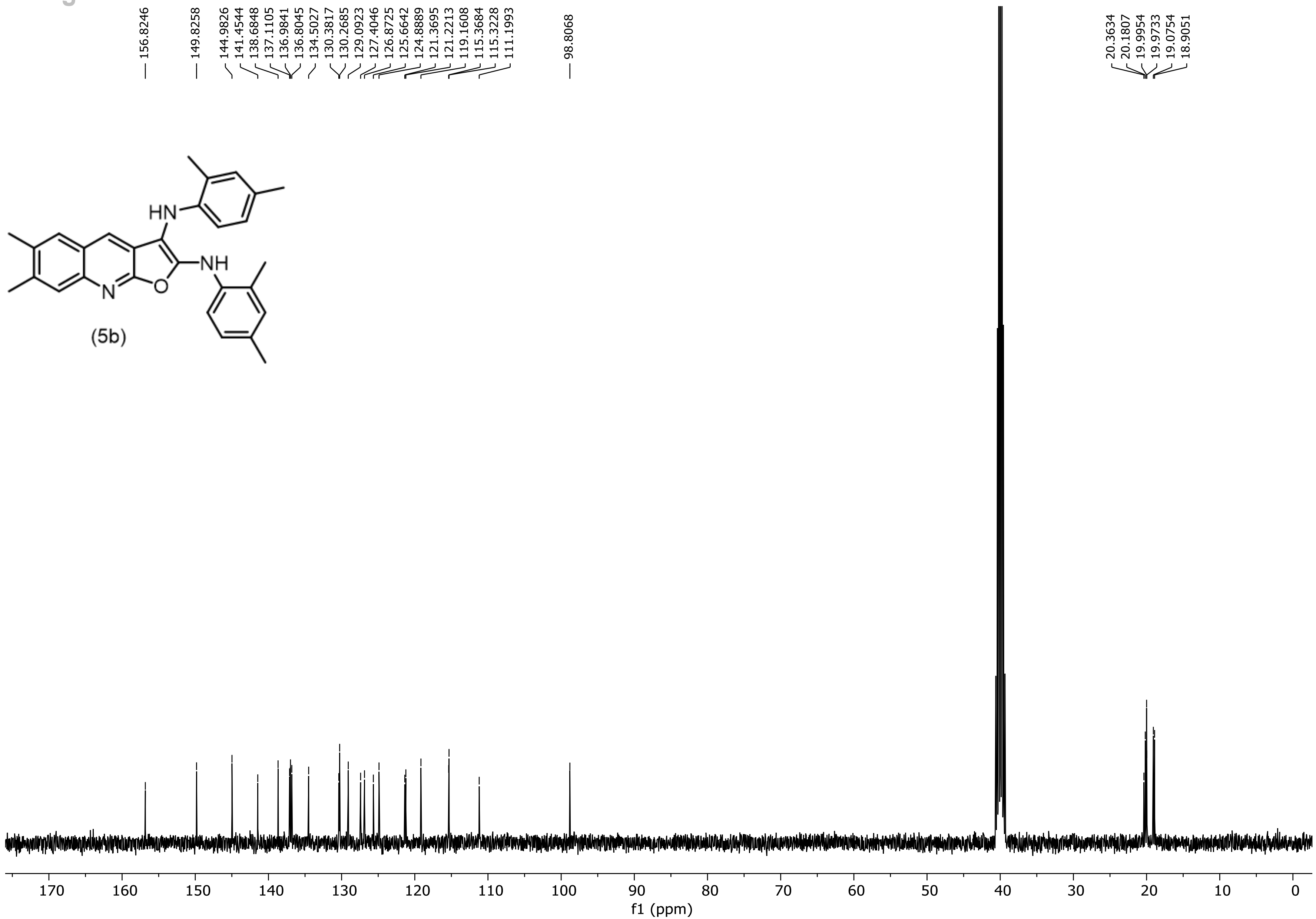


Figure S84. ¹H NMR 5b.



(5b)

Figure S85. ^{13}C NMR 5b.

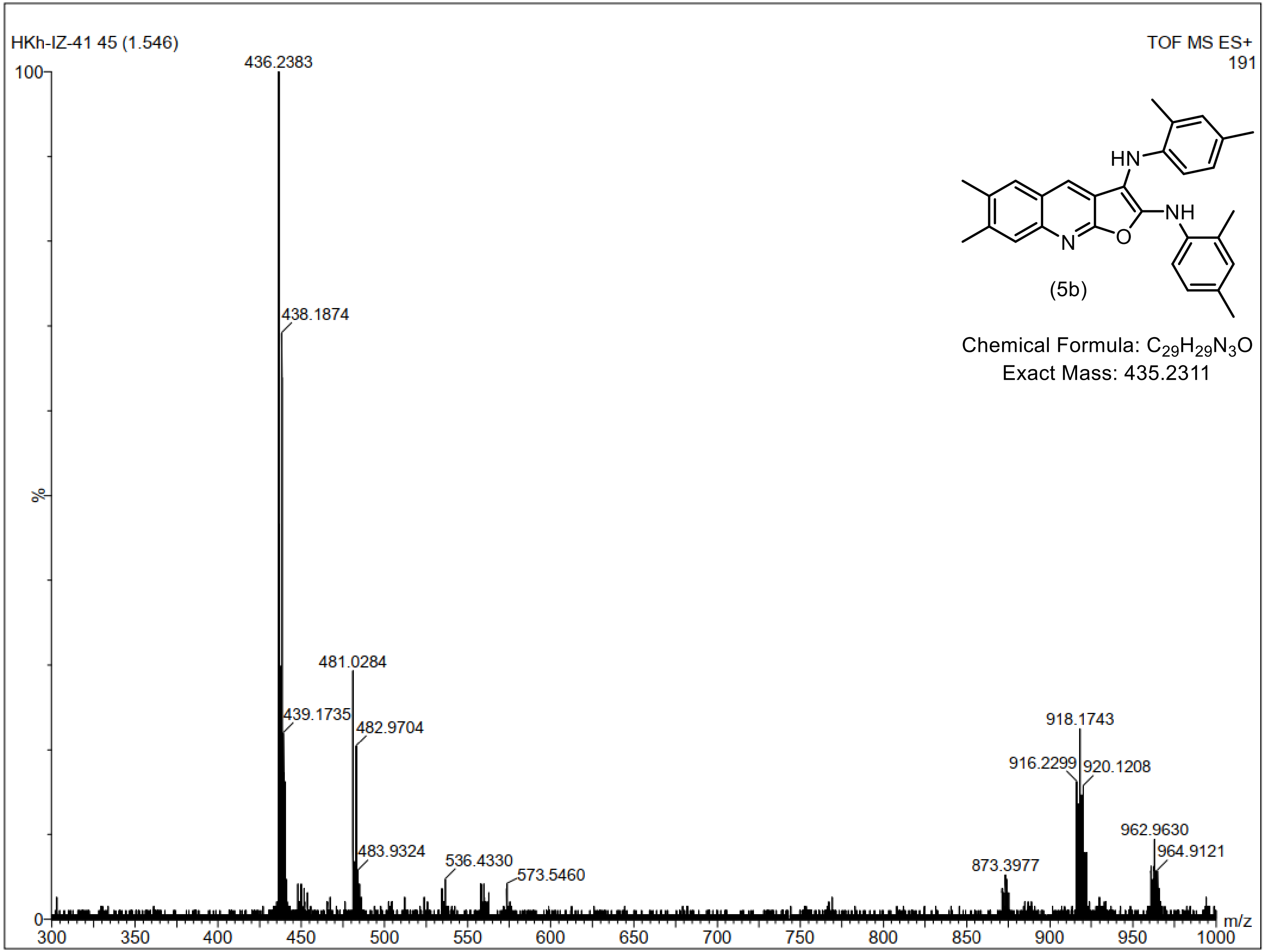


Figure S86. HRMS-ESI 5b.

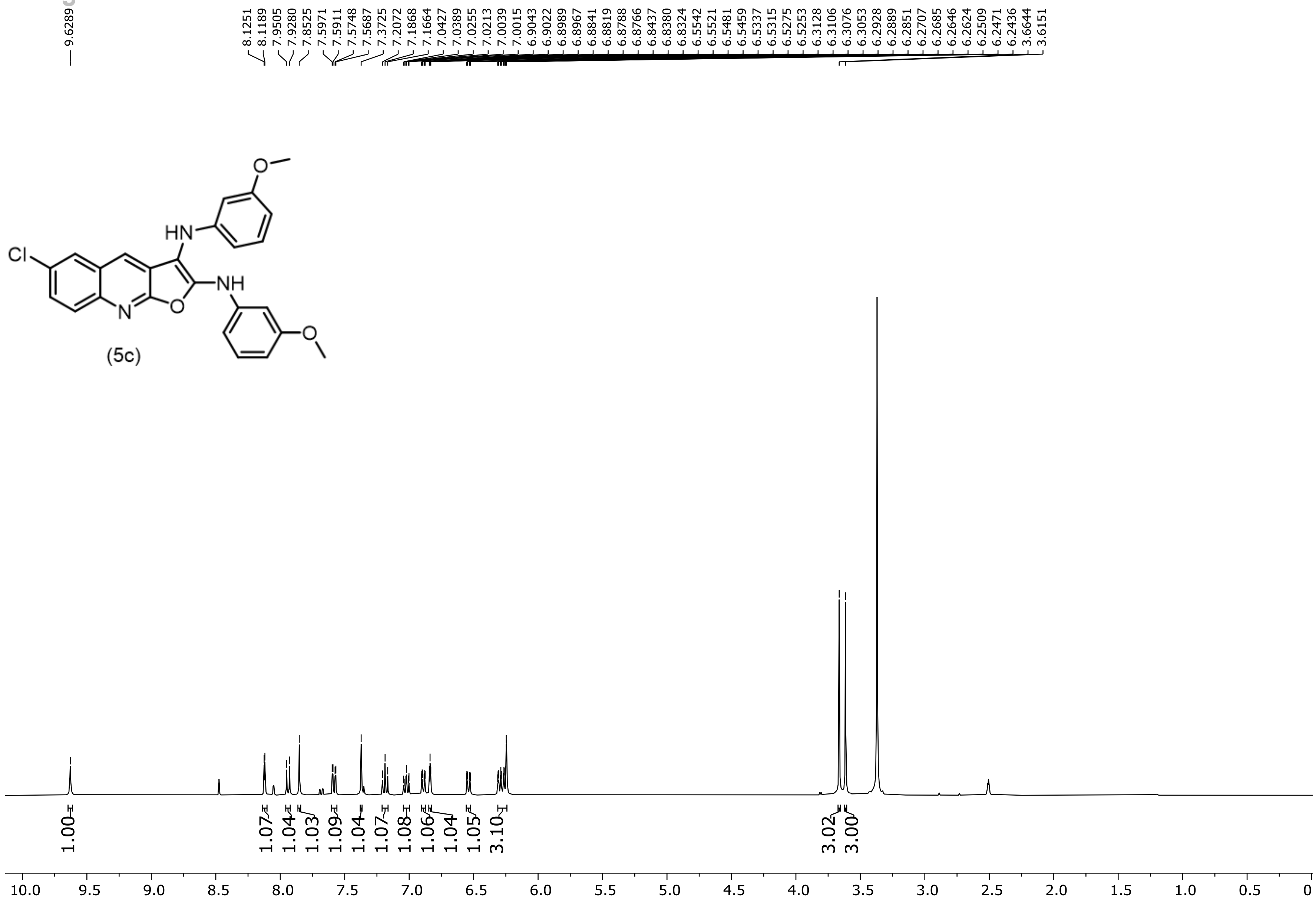


Figure S87. ^{1}H NMR 5c.

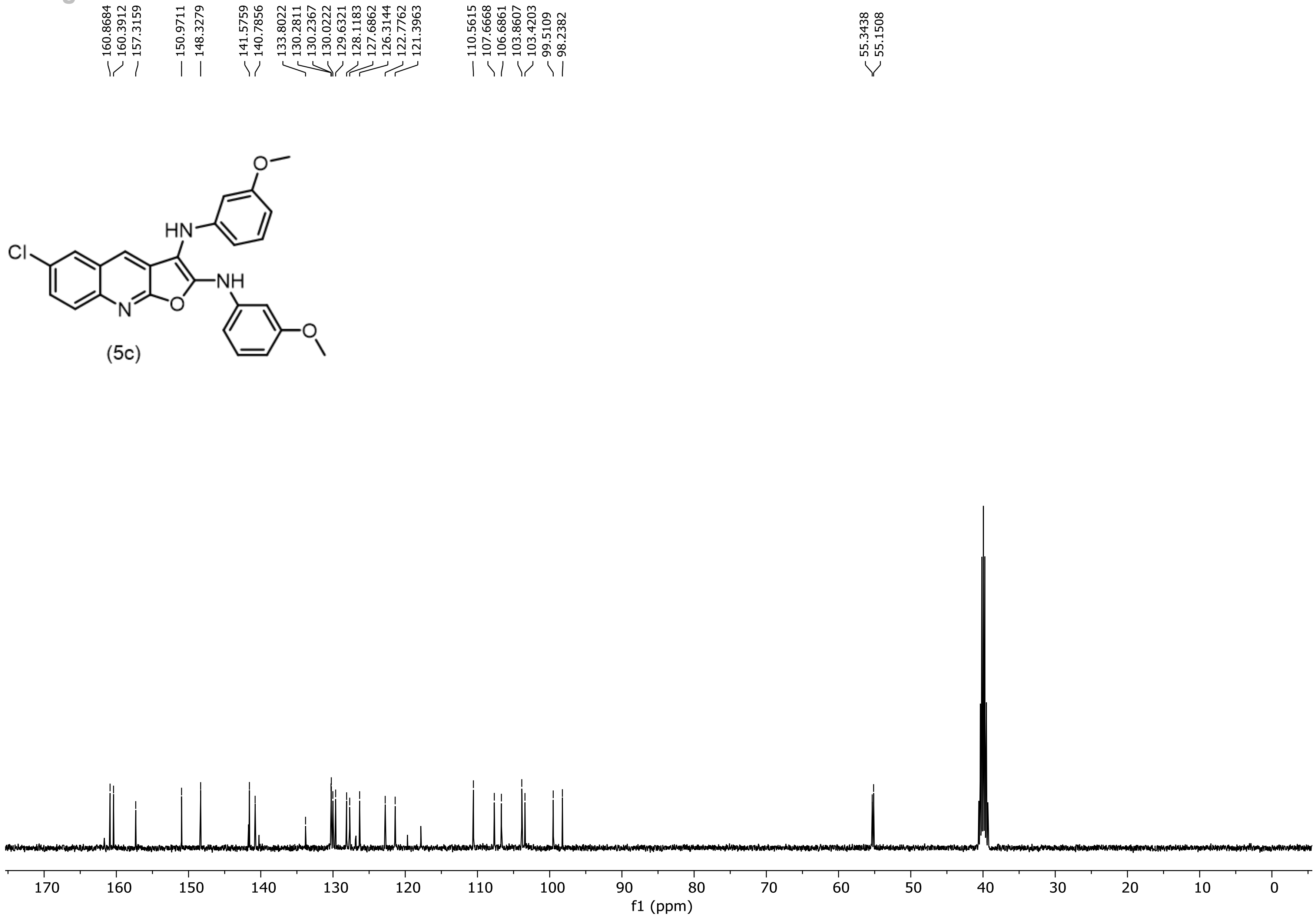


Figure S88. ^{13}C NMR 5c.

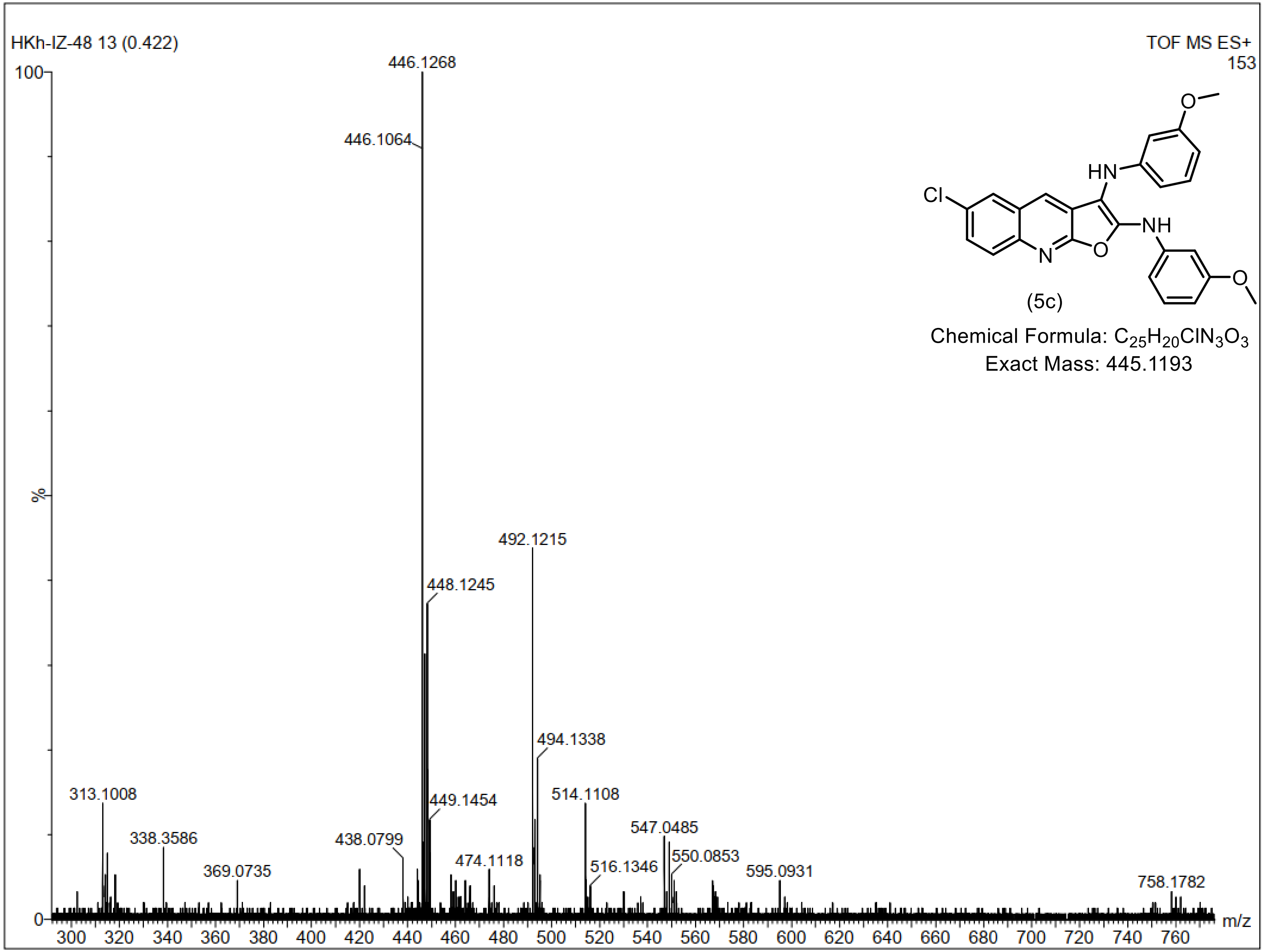


Figure S89. HRMS-ESI 5c.

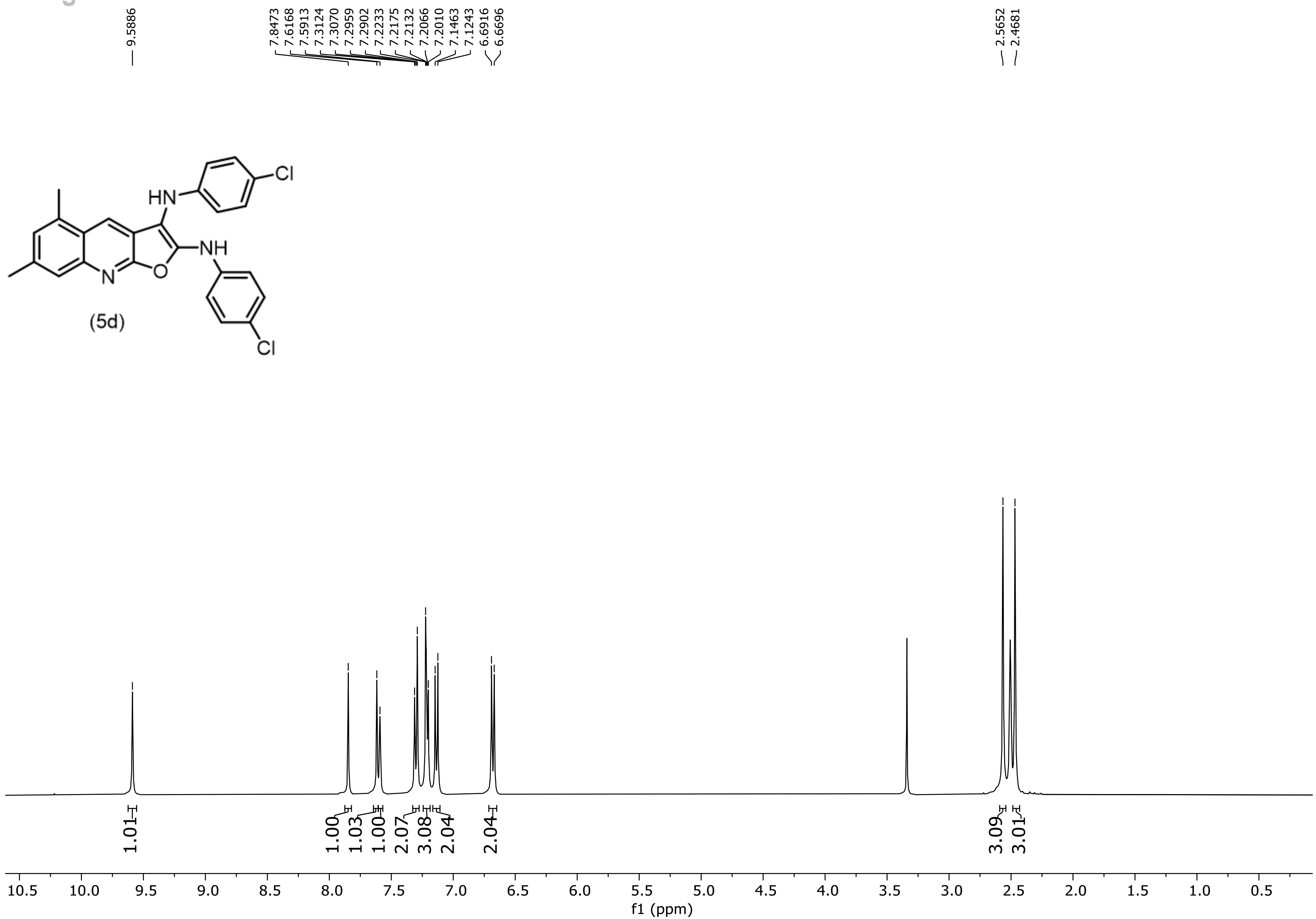


Figure S90. ^{1}H NMR 5d.

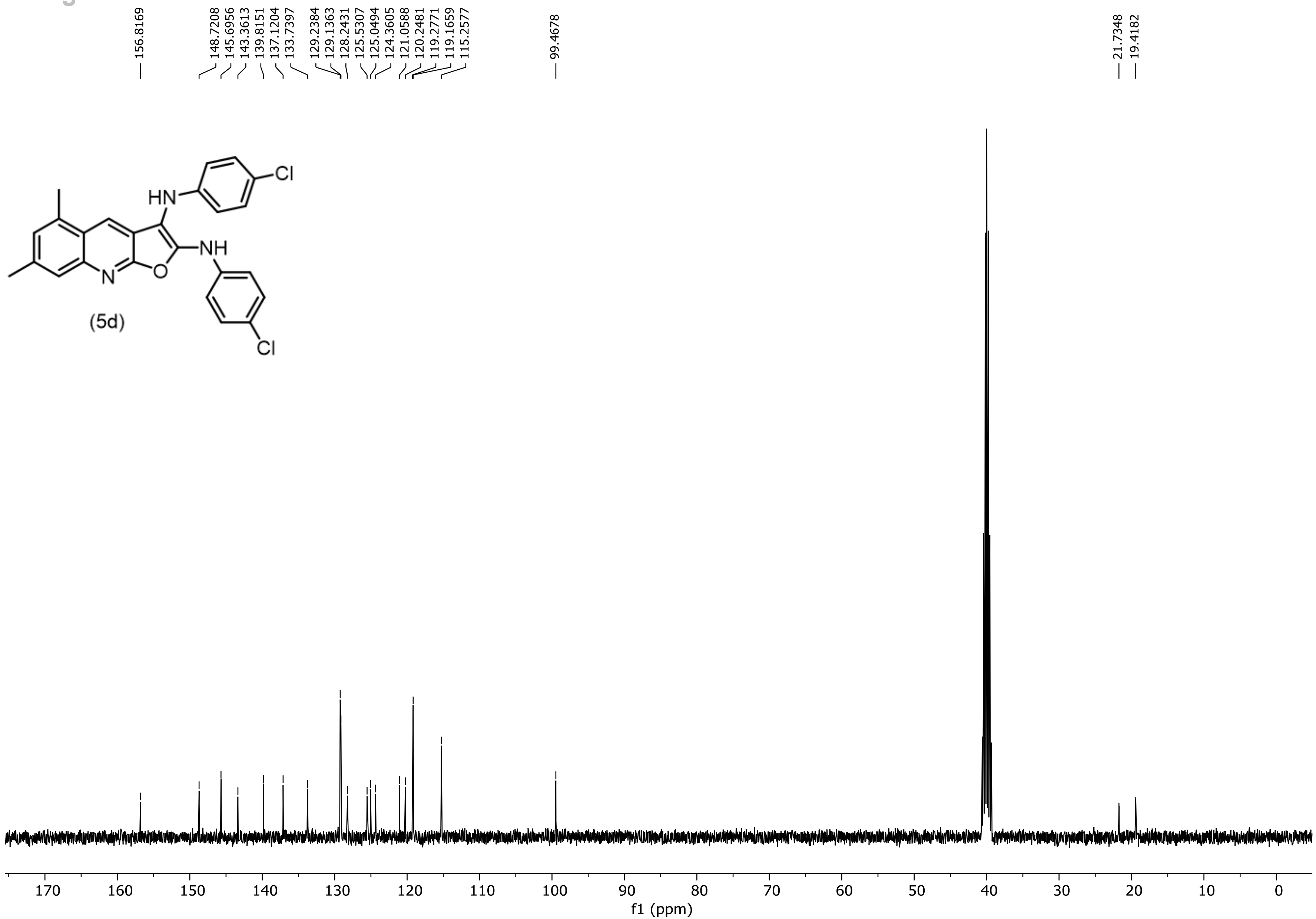


Figure S91. ^{13}C NMR 5d.

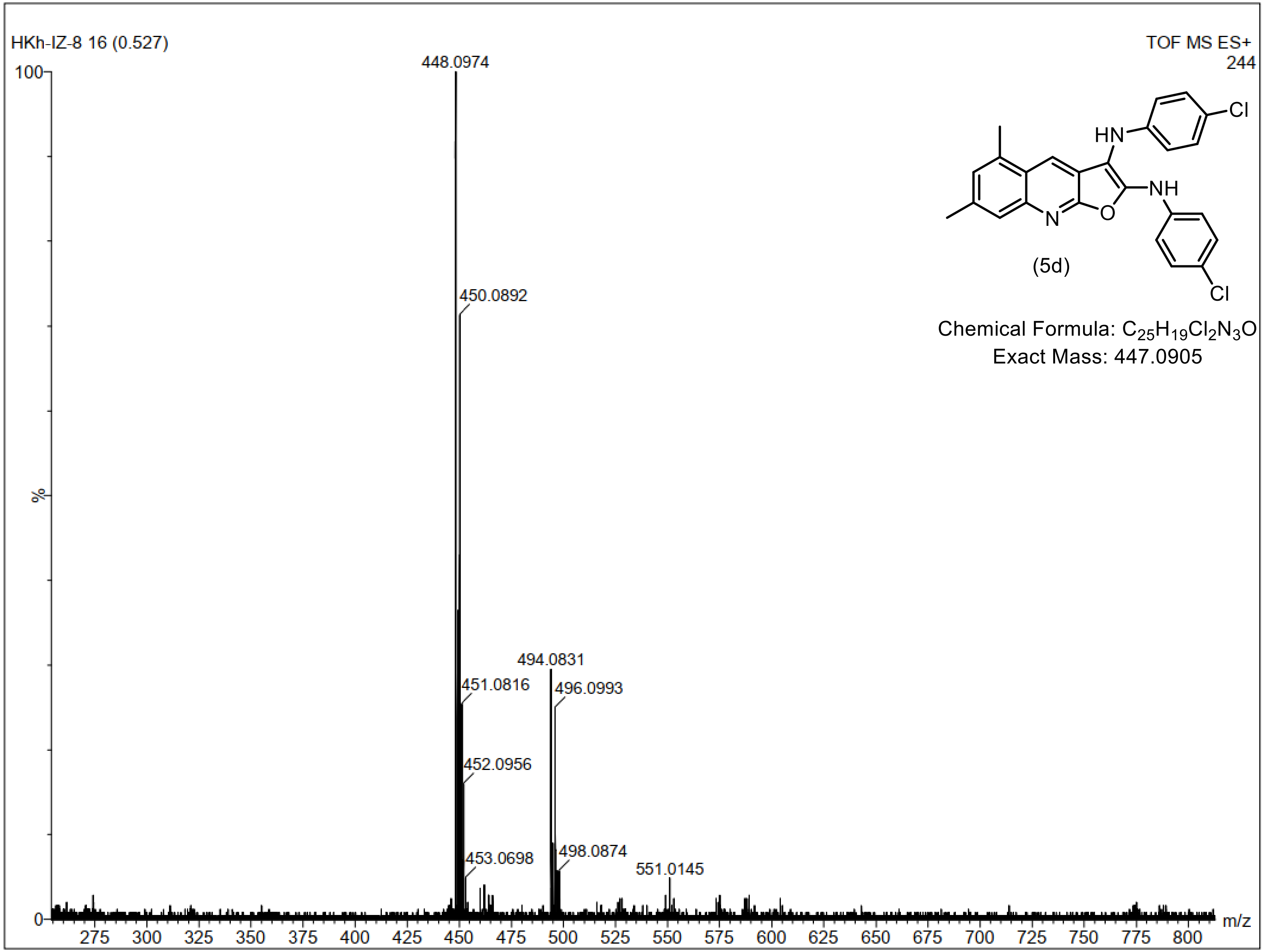


Figure S92. HRMS-ESI 5d.

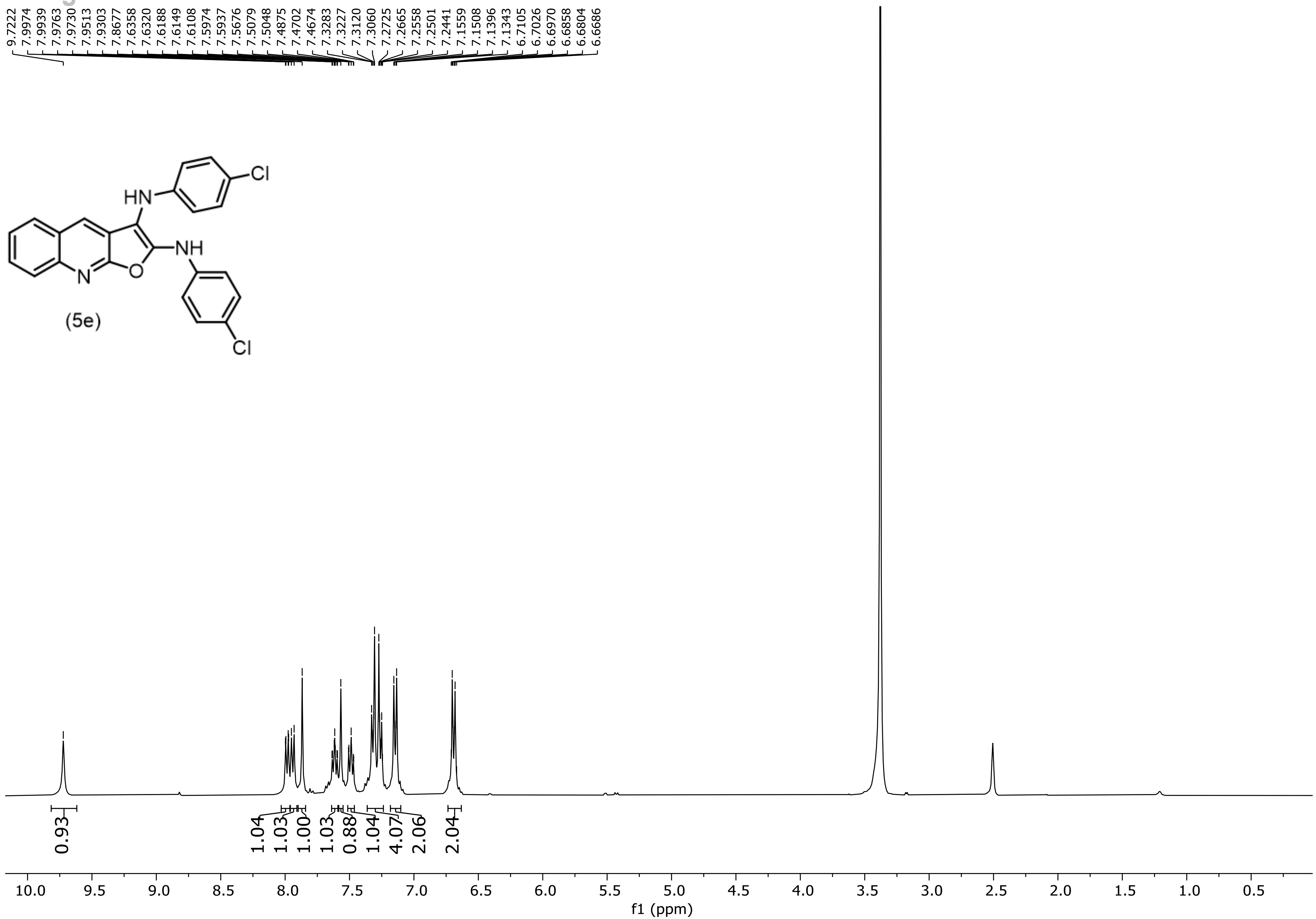
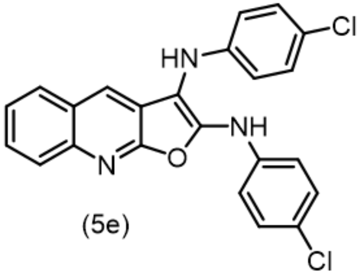


Figure S93. ^{1}H NMR 5e.



(5e)

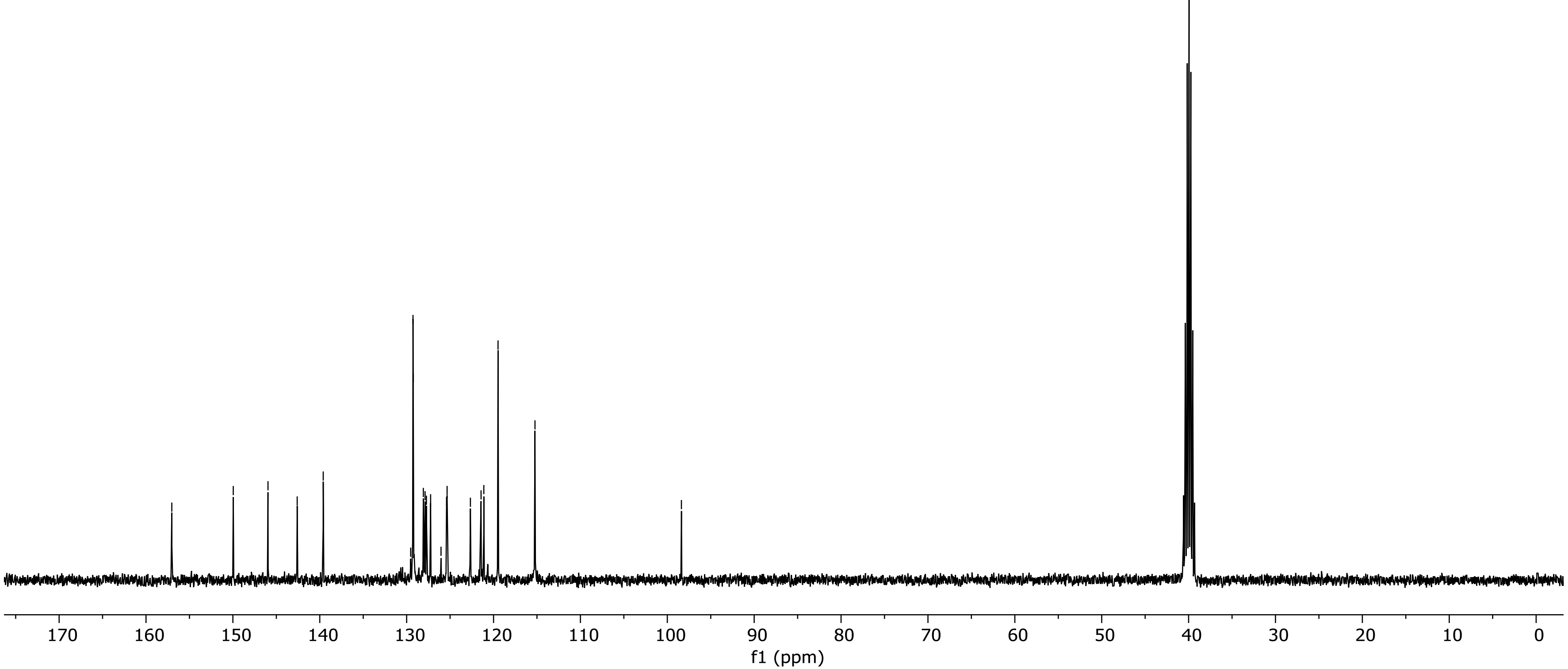


Figure S94. ^{13}C NMR 5e.

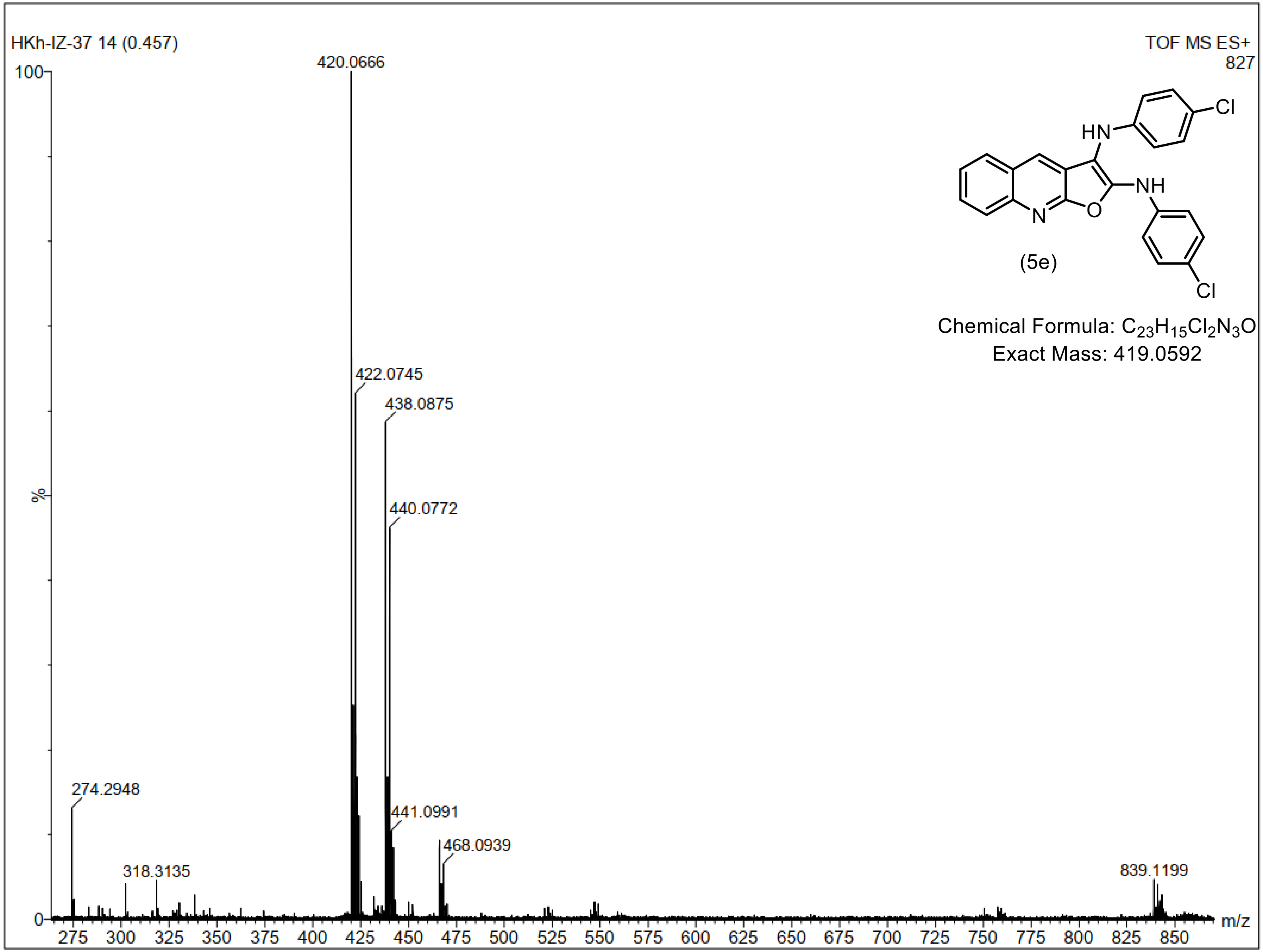


Figure S95. HRMS-ESI 5e.

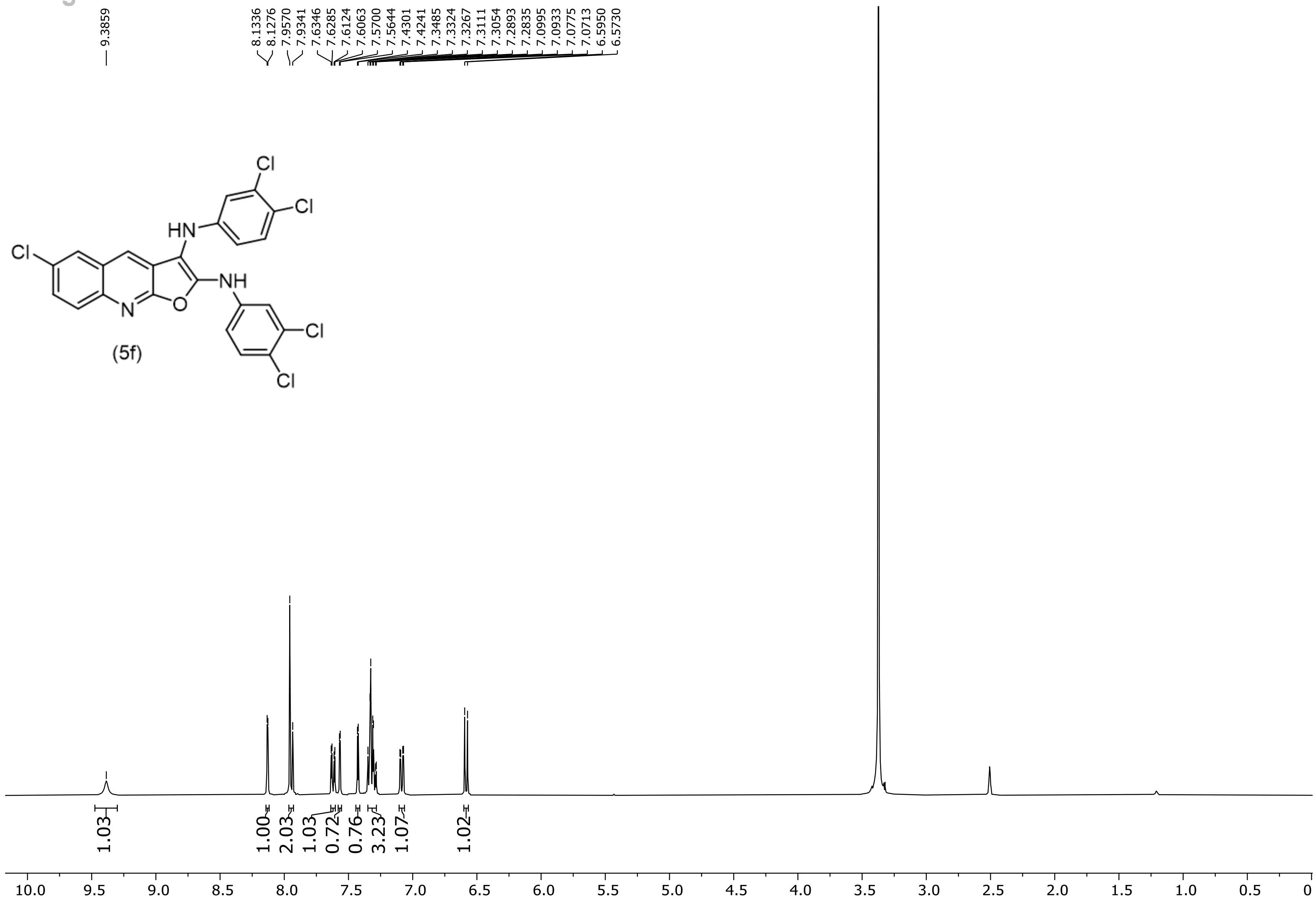


Figure S96. [1]H NMR 5f.

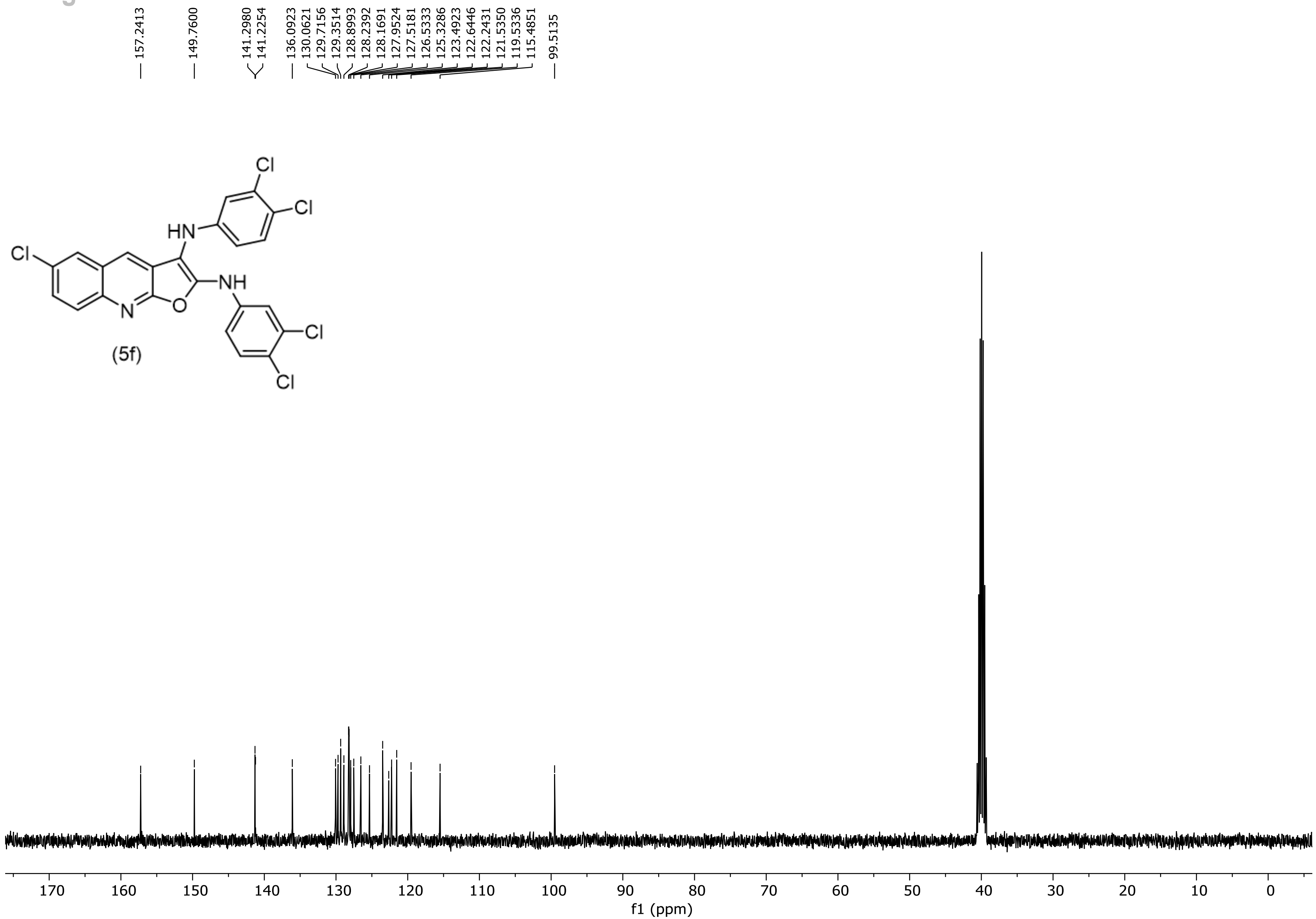


Figure S97. ^{13}C NMR 5f.

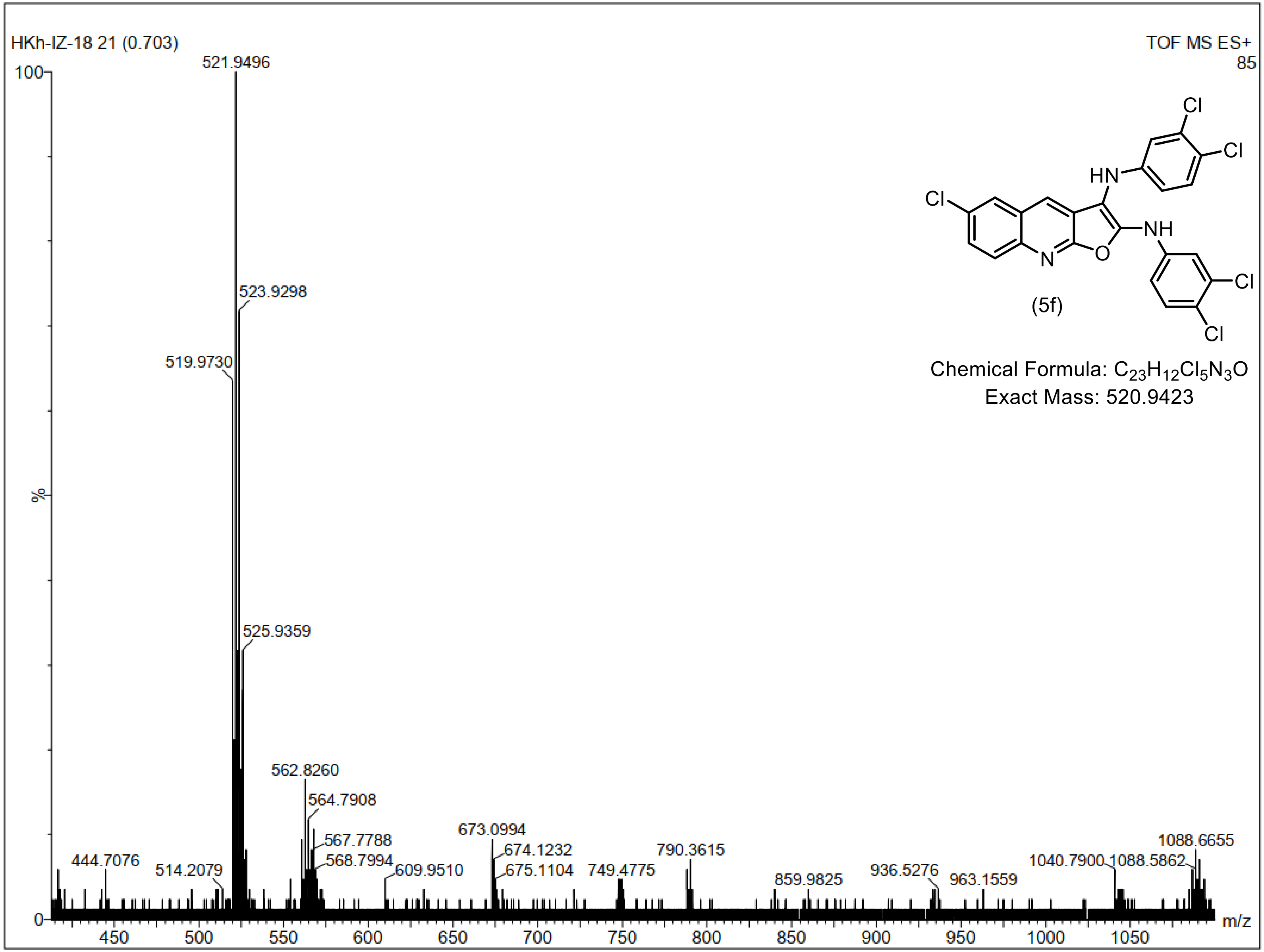


Figure S98. HRMS-ESI 5f.

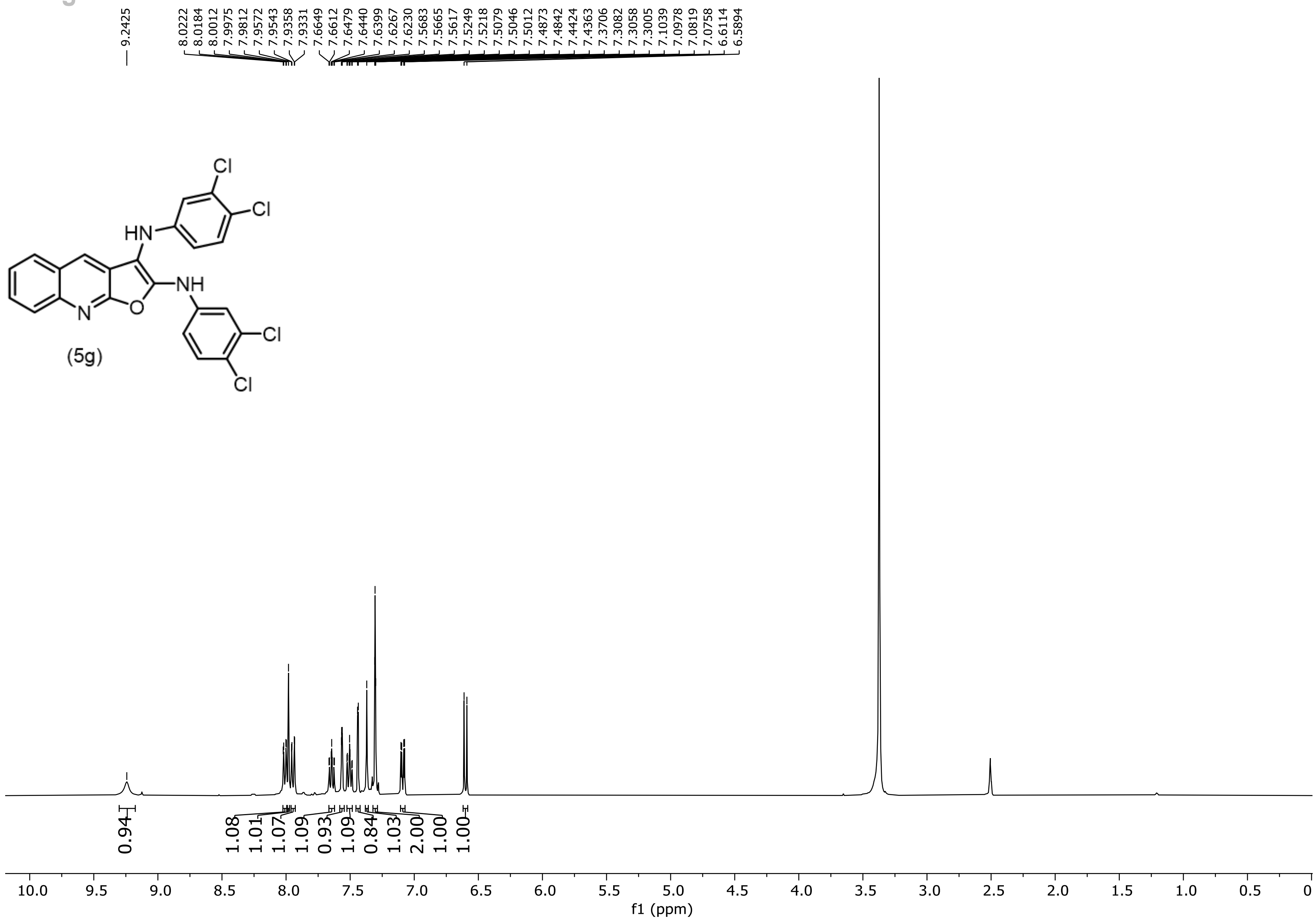


Figure S99. ^{1}H NMR 5g.

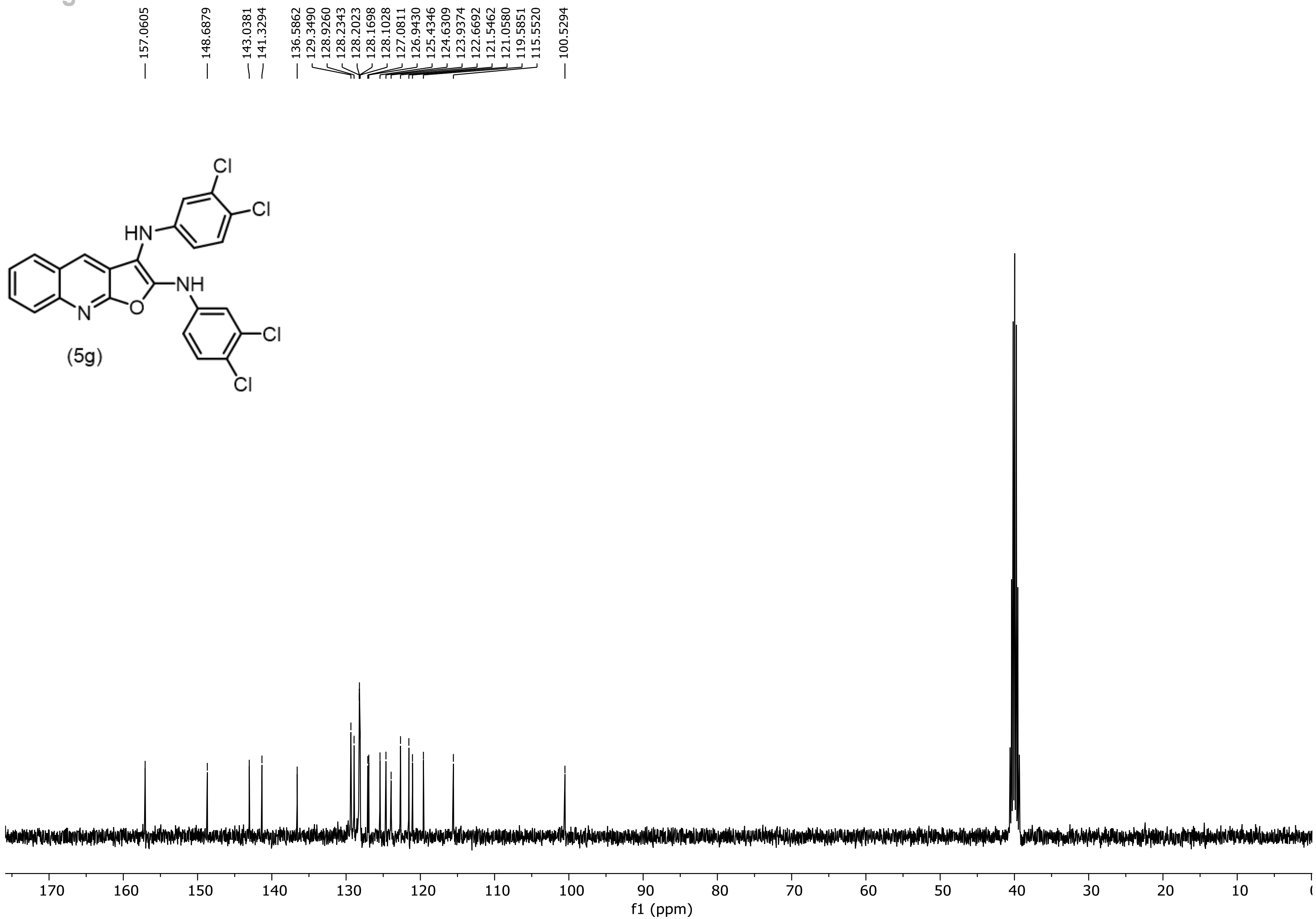


Figure S100. ^{13}C NMR 5g.

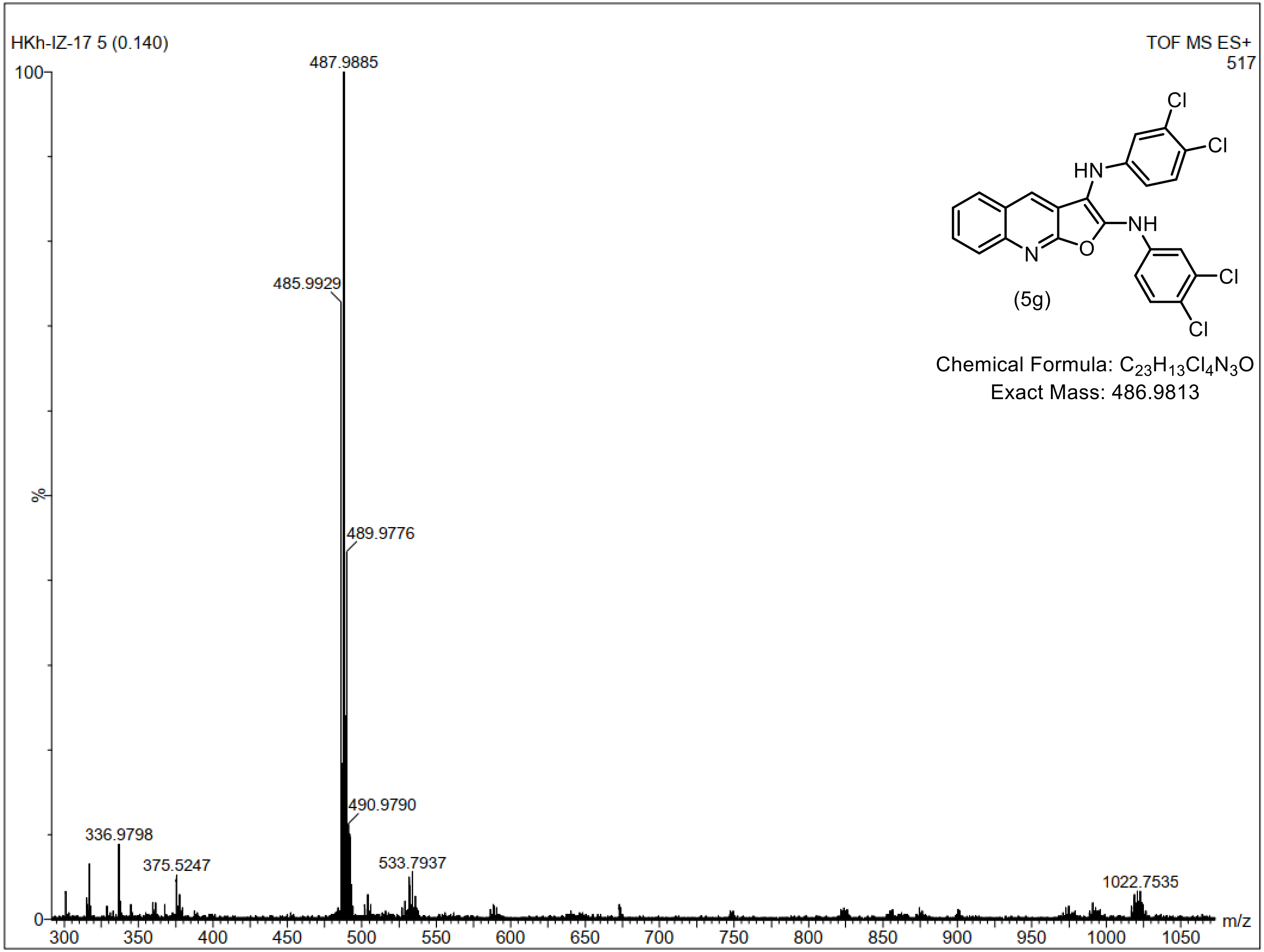


Figure S101. HRMS-ESI 5g.

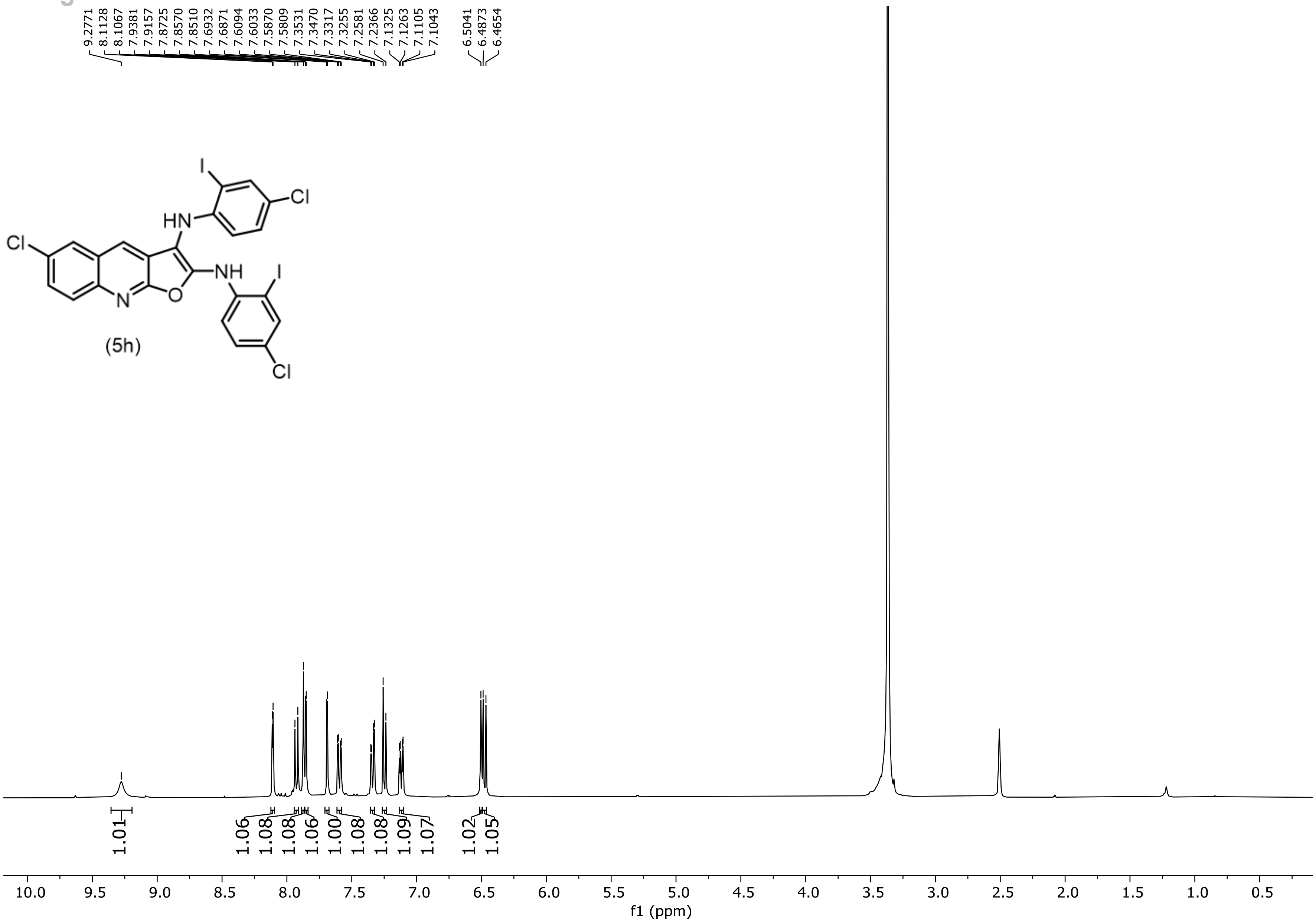


Figure S102. ^{1}H NMR 5h.

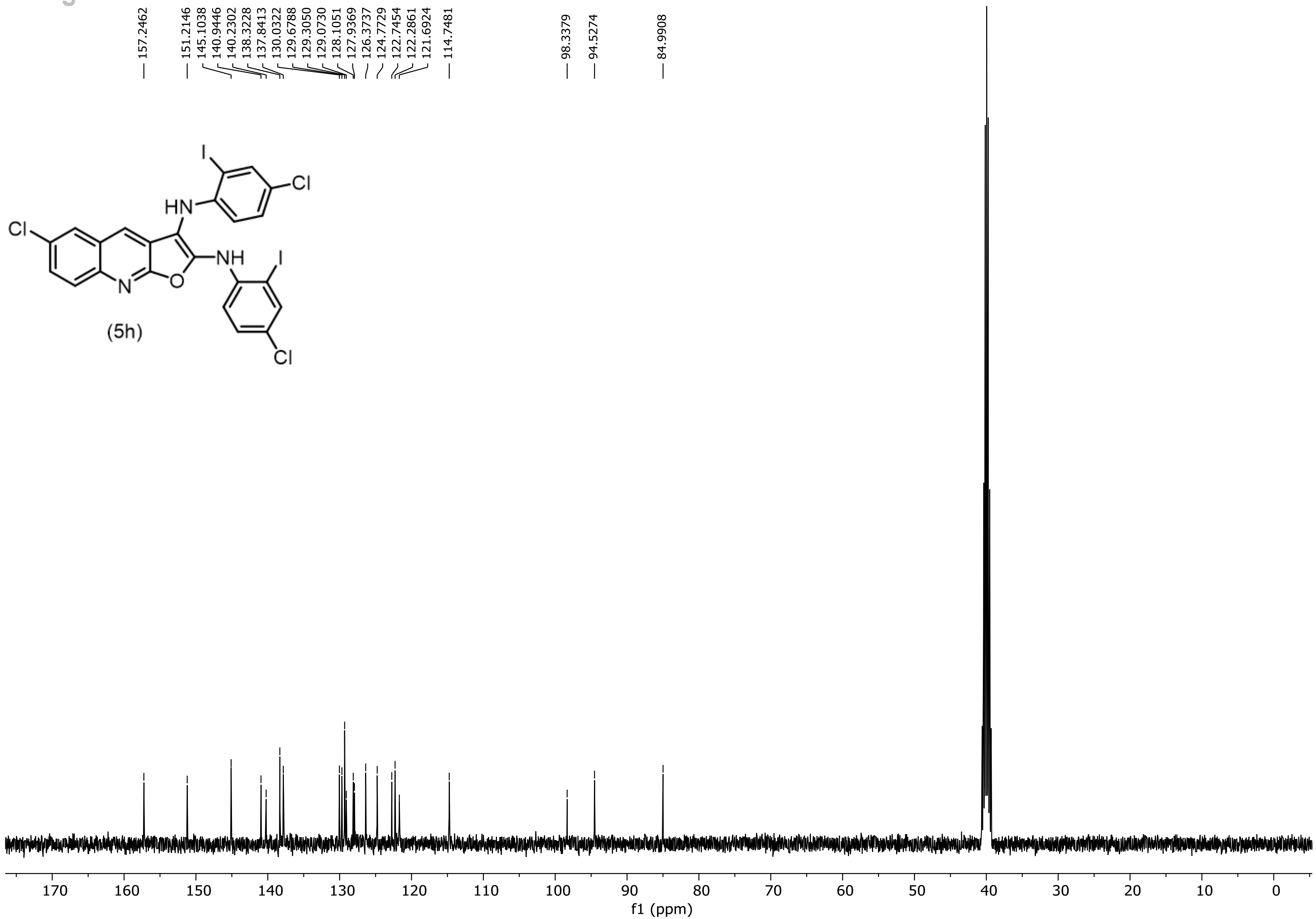


Figure S103. ^{13}C NMR 5h.

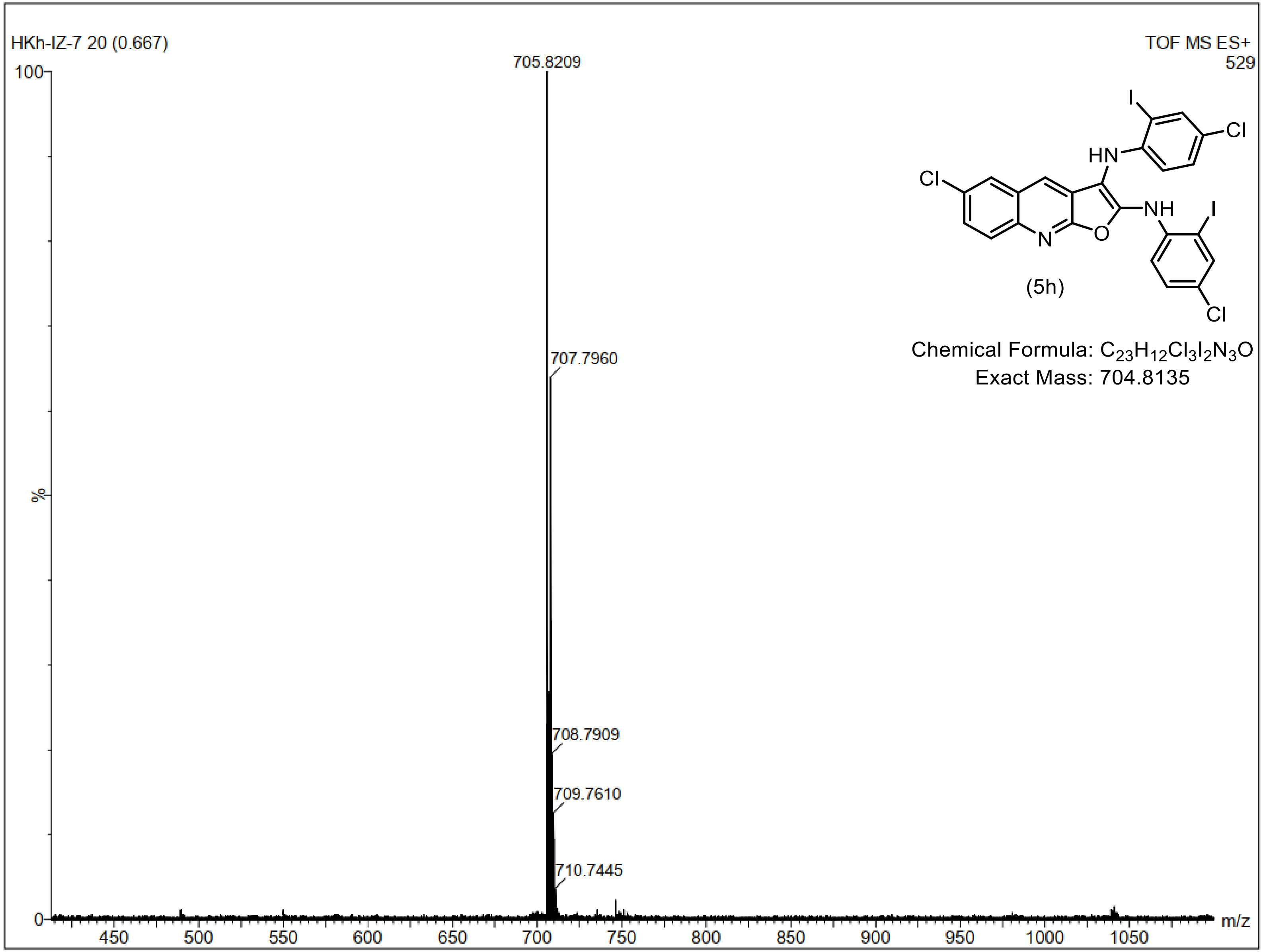


Figure S104. HRMS-ESI 5h.

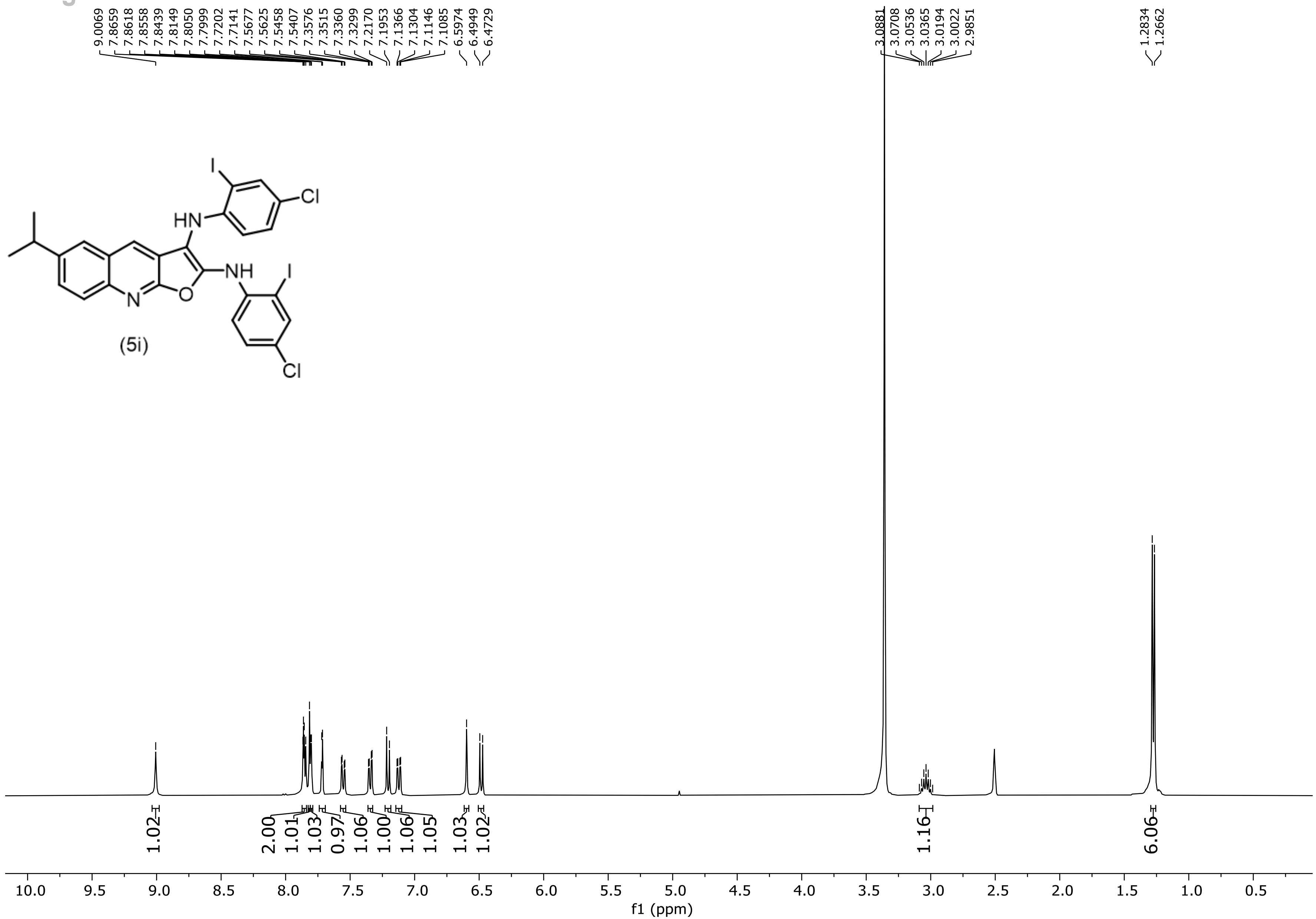


Figure S105. ^{1}H NMR 5i.

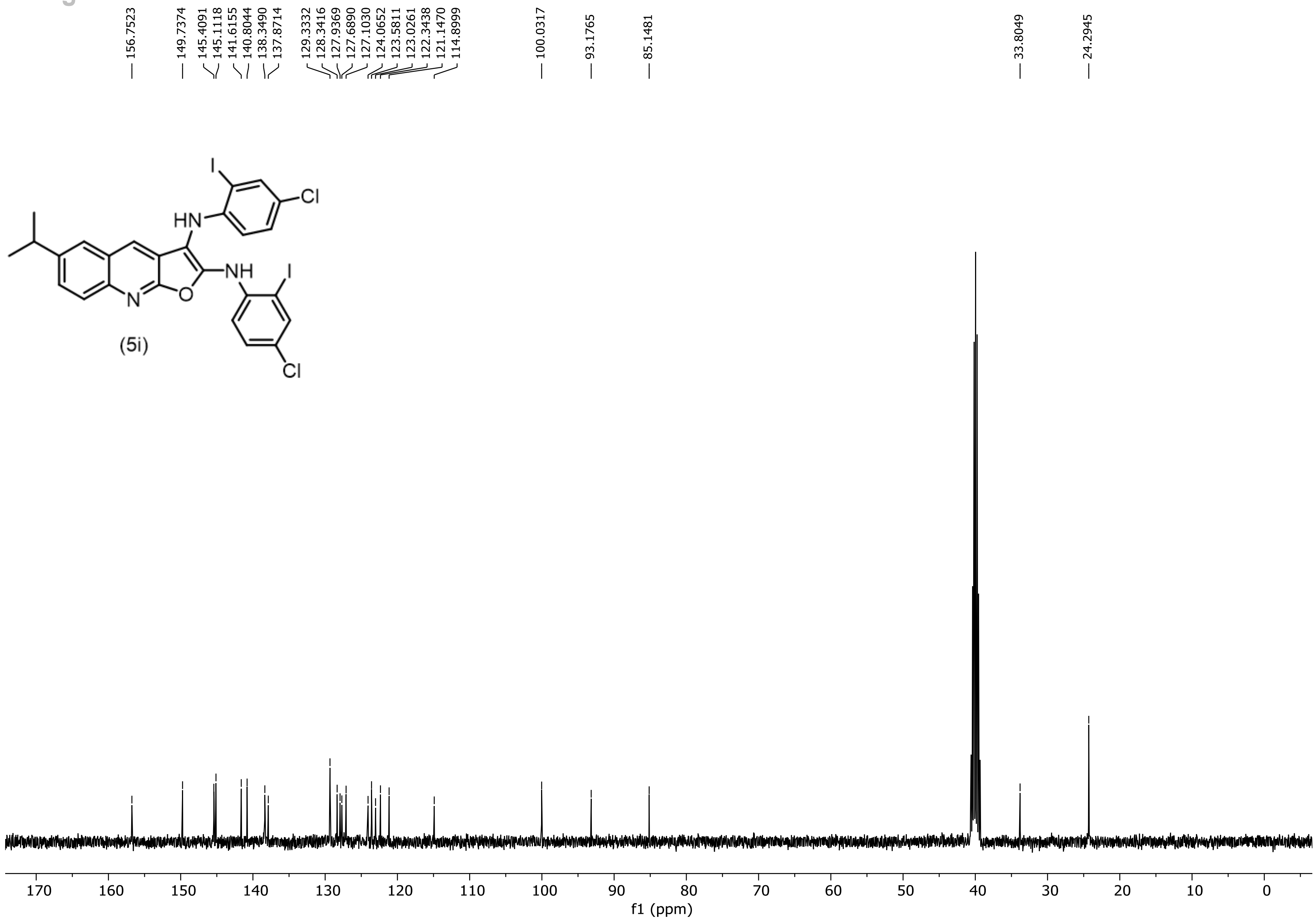


Figure S106. ^{13}**C NMR 5i.**

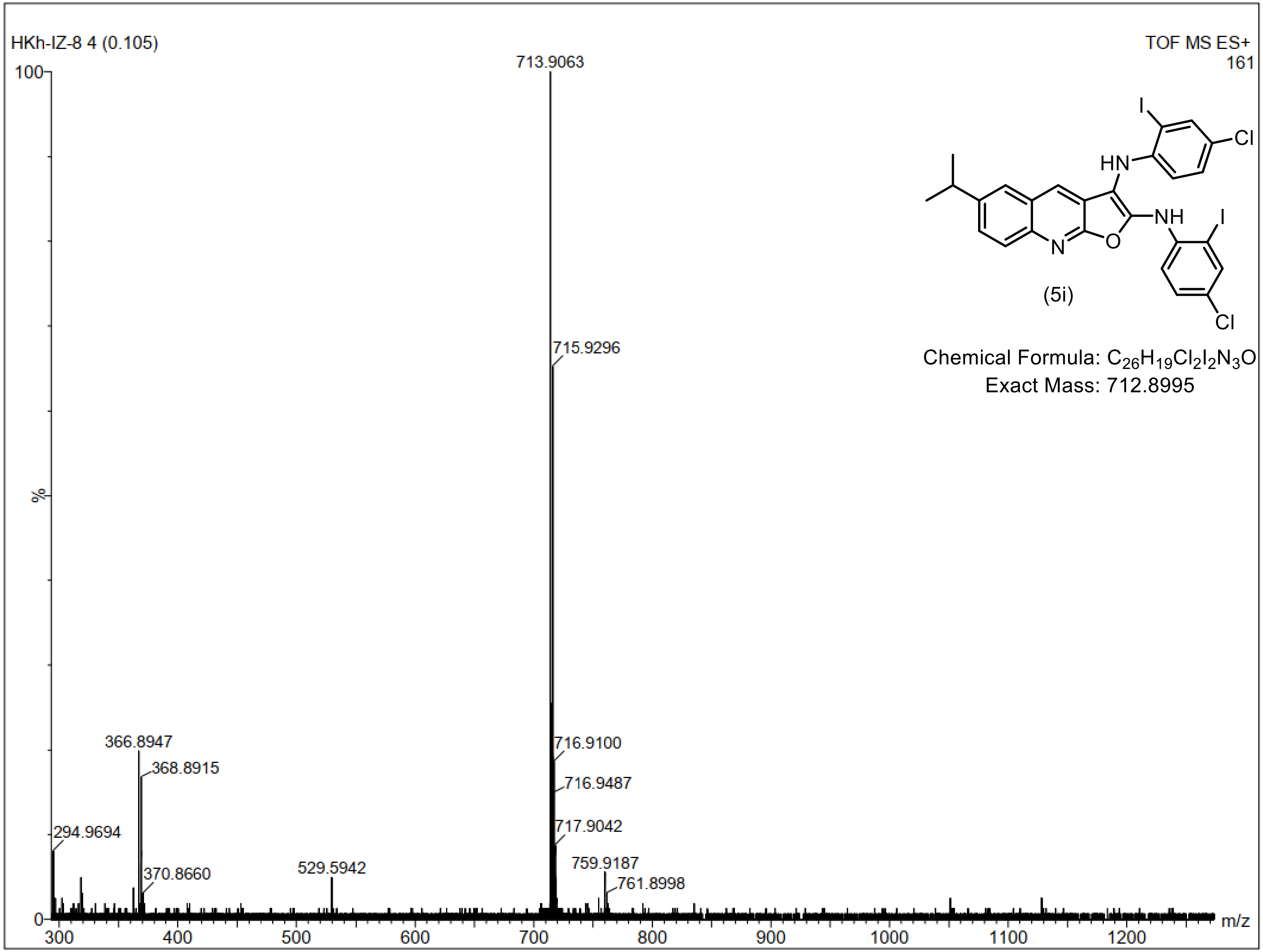


Figure S107. HRMS-ESI 5i.