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Electronic Supplementary Information

Beyond conventional Brønsted acid catalysis: Leveraging the impact of the charged moiety on the phenol to construct julolidine units

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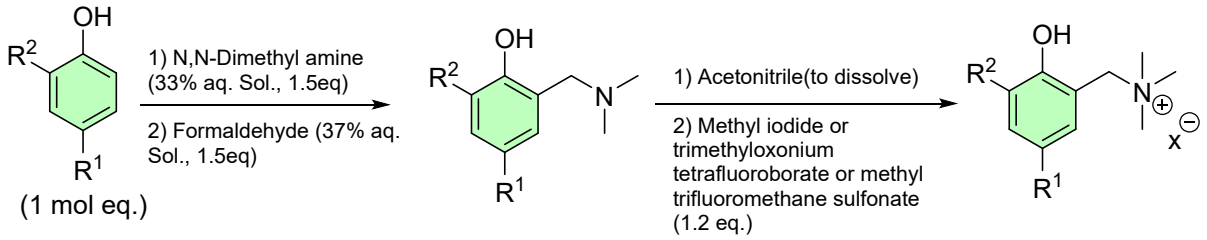
1. General Methods

Reagents and solvents were obtained from commercial sources and used as received. Air- and moisture-sensitive liquids were transferred via a syringe and a stainless-steel needle. Reactions were magnetically stirred and monitored by thin layer chromatography. All work-up and purification procedures were carried out with reagent-grade solvents under ambient atmosphere. For separation of products column chromatography was carried out using Finar 100-200 mess silica as stationary phase.

Nuclear magnetic resonance (NMR) spectra were acquired on a 500 MHz Bruker Avance III spectrometer. ^{1}H and ^{13}C NMR chemical shifts are reported in ppm and referenced to tetramethylsilane or residual solvent peaks as internal standards (for $CDCl_3$, tetramethylsilane) ppm for ^{1}H and $CDCl_3$ 77.16 ppm for ^{13}C; for DMSO-d6, 2.50 ppm for ^{1}H and 39.52 ppm for ^{13}C. NMR data are reported as follows: chemical shifts, multiplicity (s, singlet; d, doublet; dd, doublet of doublet; t, triplet; td, triplet of doublet; q, quartet; m, multiplet; br, broad signal), coupling constants (Hz), and integration. The reduced products were identified with a gas chromatography (Bruker 450-GC; equipped with a capillary column HP-5, 30m × 0.25 mm) using a flame ionization detector.

2. General procedure for catalyst synthesis[1]



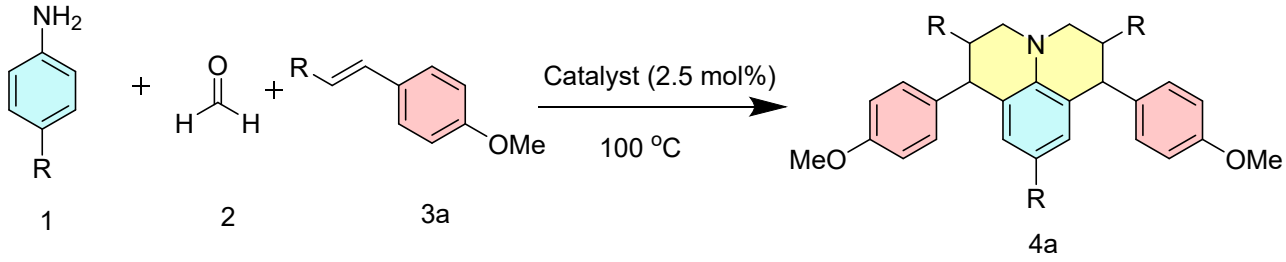
Scheme S1: General scheme for synthesis of ETP catalysts

The synthesis of phenol-alkylammonium salt followed our previously established procedure. Initially, a 1 equivalent of the desired phenol was placed in a round bottom flask. Aqueous solutions of dimethylamine (1.5 equivalents, 33% concentration) and formaldehyde (1.5 equivalents, 37% concentration) were subsequently added to the flask. The reaction mixture was then stirred at room temperature overnight. After completion, the reaction mixture underwent

extraction using a mixture of ethyl acetate and water. Subsequently, the organic solvent was removed under reduced pressure.

The resulting crude product was dissolved in acetonitrile, and either methyl iodide, trimethyloxonium tetrafluoroborate, or methyltrifluoromethane sulfonate (1.5 equivalents) was introduced. The reaction mixture was left to stir for 24 hours at room temperature. The product that precipitated during this period was filtered and washed with diethyl ether, yielding the purified product of ETPs.

3. General procedure for catalytic synthesis of julolidine using ETP



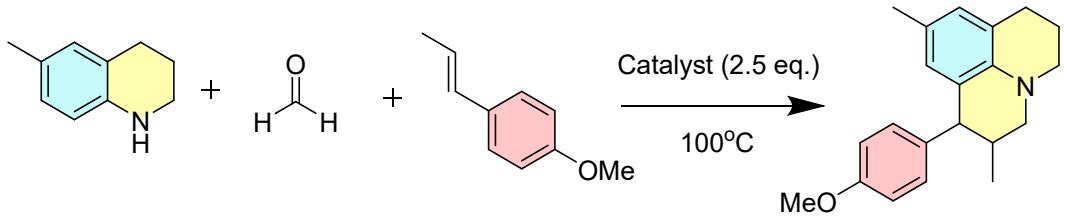
Scheme S2: General procedure catalytic synthesis of julolidine using ETP

The vial containing a mixture of aniline **1** (1.0 mmol), paraformaldehyde **2** (3.0 mmol), anethole or 4-methoxy styrene (3.0 mmol), and catalyst (2.5 mol %) was sealed and placed at 100°C under stirring for 1 h. Afterward, the reaction mixture was cooled to room temperature make a slurry in 100-200 mess silica. The obtained solid was purified by silica gel column chromatography (hexane/ dichloromethane/ethyl acetate) to afford the julolidines in high purities. All products were characterized by ^{1}H and ^{13}C NMR.

4. Procedure to find rate determining step of the reaction

The vial containing a mixture of aniline **1** (1.0 mmol), paraformaldehyde **2** (3.0 mmol), anethole (3.0 mmol), and catalyst (2.5 mol %) in toluene (2 mL) was sealed and placed at 100 °C under stirring for 1 h. Sample was taken at regular intervals (every 5 mins.) and the conversion and selectivity were determined by GCMS and plotted the graph.

5. Kinetic study of the reaction



Scheme S3: General procedure for catalytic synthesis of julolidine from 6-methyl 1,2,3,4-tetrahydroquinoline using ETP

The 6-methyl-1,2,3,4-tetrahydroquinoline is synthesised by the reported procedure.[1] The Ssynthesised 6-methyl 1,2,3,4-tetrahydroquinoline is further used for the kinetic study. 6-methyl 1,2,3,4-tetrahydroquinoline (1.0 mmol), paraformaldehyde (1.5 mmol), anethole (1.5mmol), and catalyst (2.5 mol %) and 2 mL of toluene is taken as a solvent, sealed and placed at 100 °C under stirring for 10 minutes. The sample was taken at every 2 minutes from the reaction mixture and the conversion was determined by GC. The data is used to plot the conversion vs time graph as shown in the manuscript. The slope of the graph gives the rate of the particular reaction. Then we have calculated relative rate of reaction (K_{rel}) as given in the continuing page (Calculation of K_{rel}).

NMR data of product:

^{1}H NMR (600 MHz, CHLOROFORM-D) δ 7.08 – 6.96 (m, 2H), 6.89 – 6.78 (m, 2H), 6.62 (d, J = 2.1 Hz, 1H), 6.26 (d, J = 2.2 Hz, 1H), 3.80 (s, 3H), 3.52 (d, J = 9.1 Hz, 1H), 3.19 – 3.12 (m, 1H), 3.09 – 2.97 (m, 2H), 2.87 – 2.68 (m, 4H), 2.18 (d, J = 8.3 Hz, 1H), 2.00 – 1.95 (m, 1H), 0.88 (d, J = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, CHLOROFORM-D) δ 158.00, 140.97, 138.34, 130.18, 128.82, 127.93, 125.30, 125.27, 121.64, 113.67, 56.06, 55.29, 51.33, 50.50, 35.35, 27.68, 22.40, 20.39, 18.28.

6. Kinetics study:

a) With respect to catalyst (ETP-6):

A clean vial was charged with 6-Methyltetrahydroquinoline A (0.25 mM), Formaldehyde B (0.75 mM), Anethole C (0.75 mM), and ETP-6 (2.5 mol%). Toluene (0.5 mL) was then added. The vial was placed in an oil bath and stirred at 100 °C. Every 2 minutes, a 20 µL sample was taken from the vial, to which 20 µL of diethyl ether was added, and the mixture was centrifuged. The liquid portion was then subjected to GC analysis. Multiple experiments were conducted to determine the reaction rate at various catalyst concentrations (1.5 mol%, 2 mol%, 3 mol%, and 3.5 mol%), while keeping all other parameters constant. The data obtained were plotted as shown in Fig. S1a.

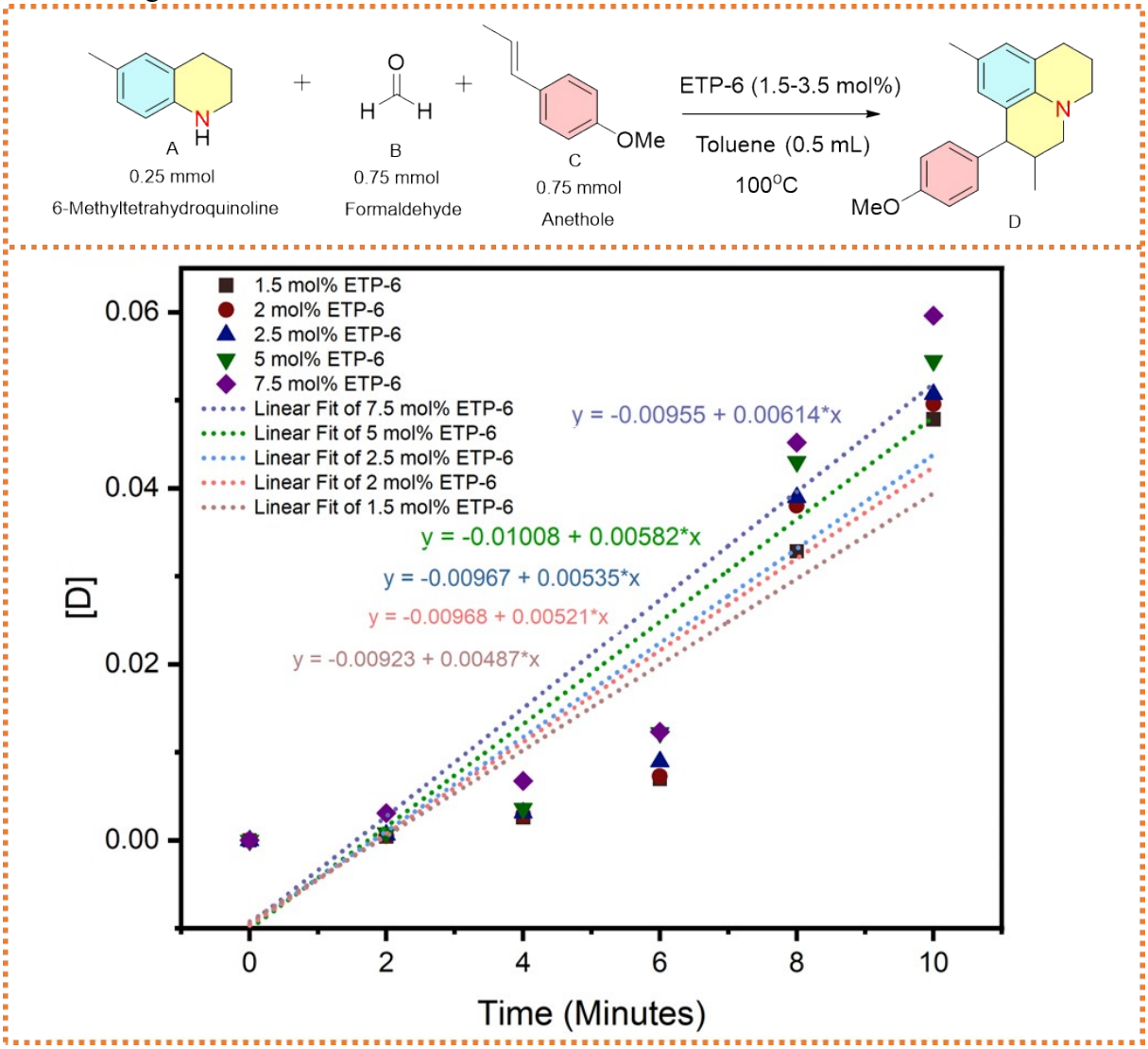


Fig S1a. Plot of [D] versus Time; reaction conditions: A (fixed at 0.25 mM), B (fixed at 0.75 mM), C (fixed at 0.75 mM) and ETP-6 (variable from 1.5 mol % to 7.5 mol %), Toluene (0.5 mL), 100°C.

b) With respect to 6-Me-THQ:

A clean vial was charged with 6-Methyltetrahydroquinoline A (0.25 mM), Formaldehyde B (0.75 mM), Anethole C (0.75 mM), and ETP-6 (2.5 mol%). Toluene (0.5 mL) was then added. The vial was placed in an oil bath and stirred at 100 °C. Every 2 minutes, a 20 µL sample was taken from the vial, to which 20 µL of diethyl ether was added, and the mixture was centrifuged. The liquid portion was then subjected to GC analysis. Multiple experiments were conducted to determine the reaction rate at various 6-Methyltetrahydroquinoline concentrations (0.15 mM, 0.20 mM, 0.30 mM, and 0.35 mM), while keeping all other parameters constant. The data obtained were plotted as shown in Fig. S1b.

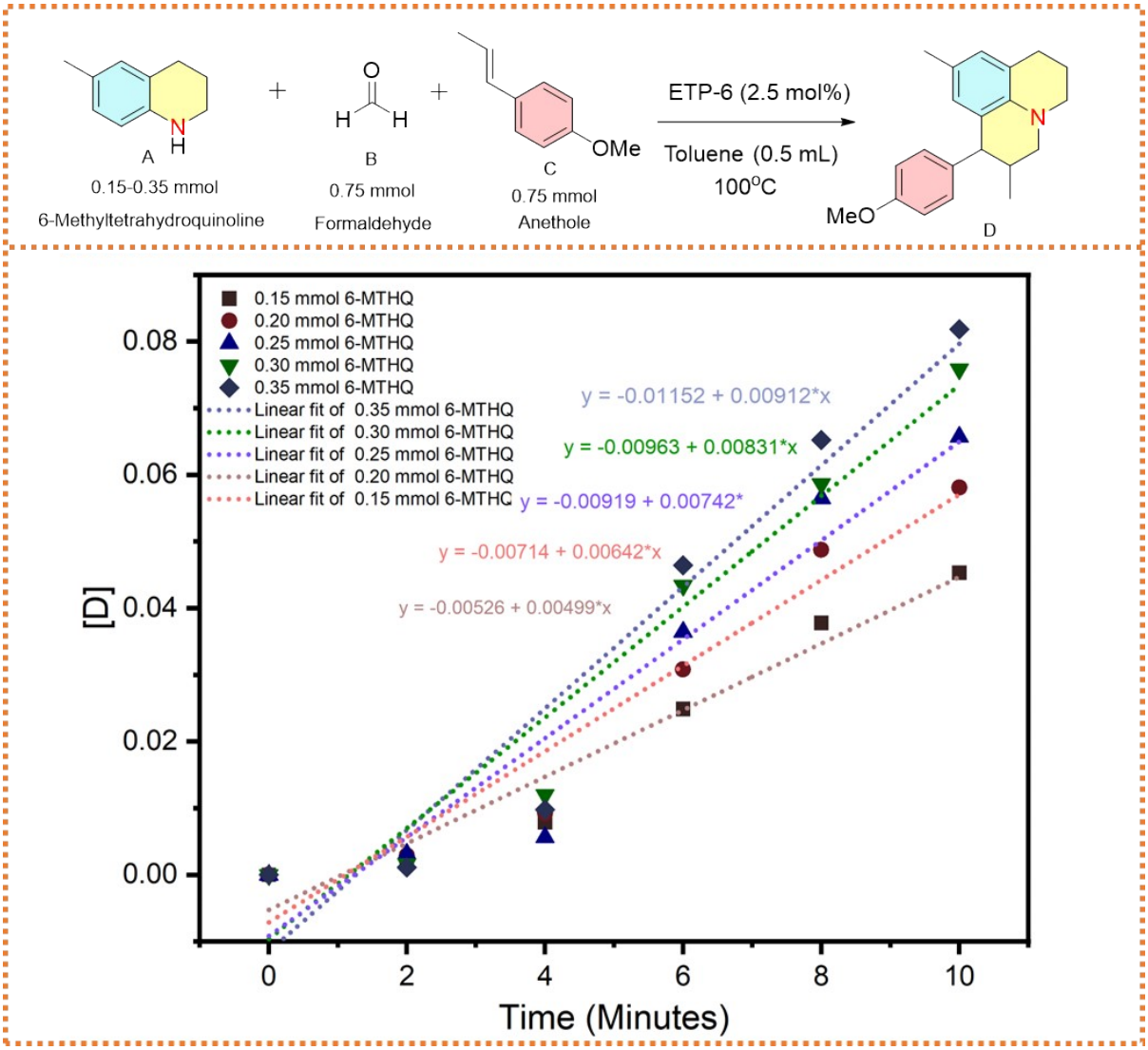


Fig S1b. Plot of [D] versus Time; reaction conditions: A (variable from 0.15 mM to 0.35 mM), B (fixed at 0.75 mM), C (fixed at 0.75 mM) and ETP-6 (fixed at 2.5 mol%), Toluene (0.5 mL) 100°C.

c) With respect to Formaldehyde :

A clean vial was charged with 6-Methyltetrahydroquinoline A (0.25 mM), Formaldehyde B (0.75 mM), Anethole C (0.75 mM), and ETP-6 (2.5 mol%). Toluene (0.5 mL) was then added. The vial was placed in an oil bath and stirred at 100 °C. Every 2 minutes, a 20 µL sample was taken from the vial, to which 20 µL of diethyl ether was added, and the mixture was centrifuged. The liquid portion was then subjected to GC analysis. Multiple experiments were conducted to determine the reaction rate at various Formaldehyde concentrations (0.65 mM, 0.70 mM, 0.80 mM, and 0.85 mM), while keeping all other parameters constant. The data obtained were plotted as shown in Fig. S1c.

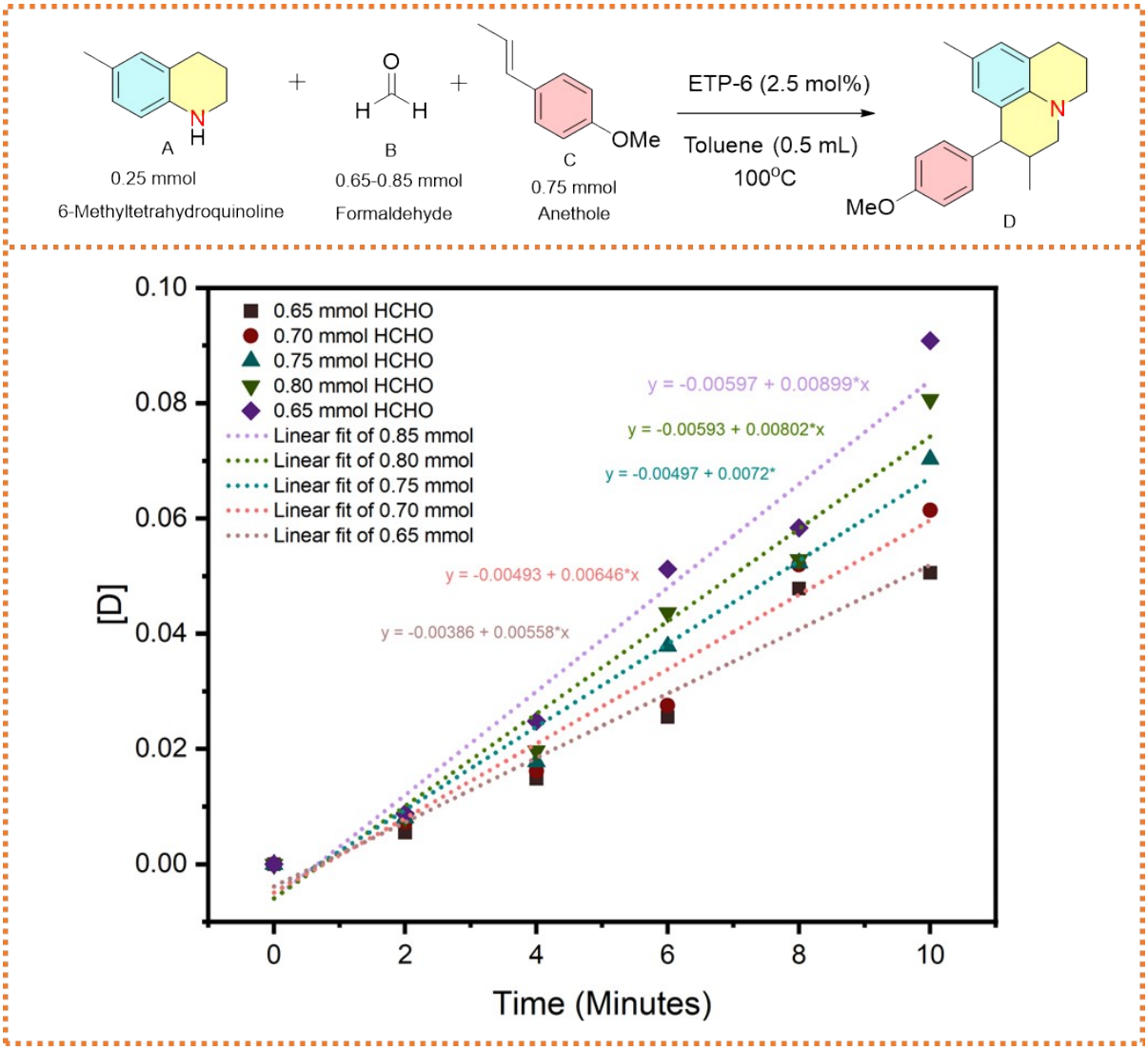


Fig S1c. Plot of [D] versus Time; reaction conditions: A (fixed at 0.25 mM), B (variable from 0.65 mM to 0.85 mM), C (fixed at 0.75 mM) and ETP-6 (fixed at 2.5 mol%), Toluene (0.5 mL), 100°C.

d) With respect to Anethole:

A clean vial was charged with 6-Methyltetrahydroquinoline A (0.25 mM), Formaldehyde B (0.75 mM), Anethole C (0.75 mM), and ETP-6 (2.5 mol%). Toluene (0.5 mL) was then added. The vial was placed in an oil bath and stirred at 100 °C. Every 2 minutes, a 20 µL sample was taken from the vial, to which 20 µL of diethyl ether was added, and the mixture was centrifuged. The liquid portion was then subjected to GC analysis. Multiple experiments were conducted to determine the reaction rate at various Formaldehyde concentrations (0.65 mM, 0.70 mM, 0.80 mM, and 0.85 mM), while keeping all other parameters constant. The data obtained were plotted as shown in Fig. S1d.

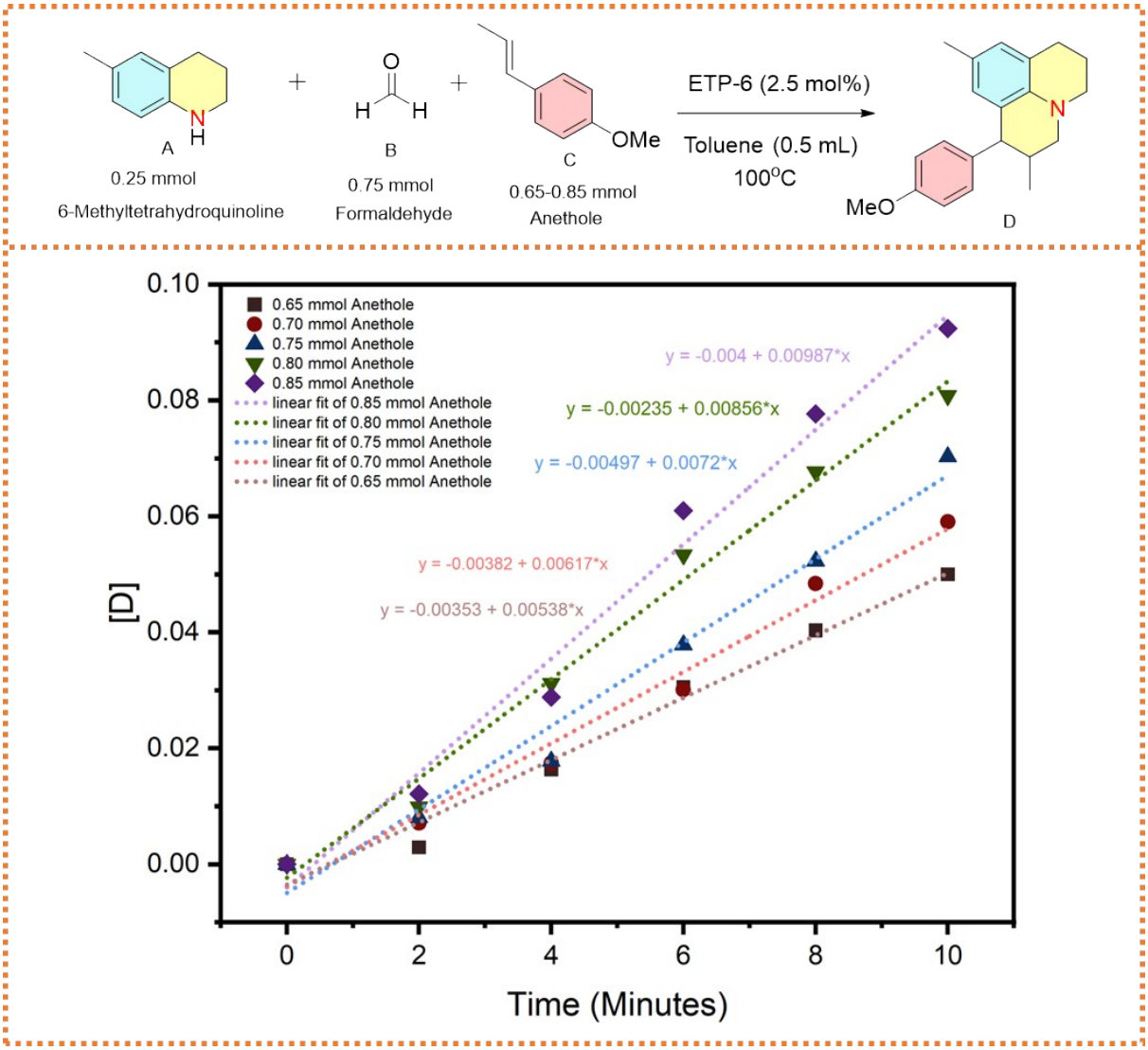


Fig S1d. Plot of [D] versus Time; reaction conditions: A (fixed at 0.25 mM), B (fixed at 0.75 mM), C (variable from 0.65 mM to 0.85 mM) and ETP-6 (fixed at 2.5 mol%), Toluene (0.5 mL) 100°C.

7. H-Bonding study of electrostatically tuned phenol using ^{31}P NMR spectra[2]

To conduct the titration using ETP-6, we initiated the process by dissolving 10 mg (equivalent to 0.0458 mmol) of n-Bu_3PO in a minimal amount of CCl_4. This solution was then carefully transferred into a 1 mL volumetric flask and diluted up to the mark, resulting in what we referred to as "solution A." In a separate 1 mL volumetric flask, we added 32.60 mg (0.0916 mmol) of catalyst and filled the flask up to the line with CCl_4, creating "solution B."

For the NMR analysis, we prepared an NMR tube containing 100 µL of solution A, to which we added 400 µL of CCl_4. The resulting mixture was inverted twice and put the reference tube in this tube separately containing phosphoric acid as a reference standard. An initial NMR spectrum was acquired to establish the ^{31}P chemical shift of n-Bu_3PO.

Subsequently, prepared another NMR tube by adding 100 µL of solution A. To this tube, carefully introduced 50 µL of solution B using a microsyringe. Then added 350 µL of CCl_4 to achieve a total solution volume of 500 µL. The resulting mixture was inverted twice and put the reference tube in this tube separately containing phosphoric acid as a reference standard before obtaining the NMR spectrum, which served as the NMR of 1 equivalent of ETP-6 with the catalyst. Following this procedure, repeated the steps to create solutions for 2, 3, 4, and 5 equivalents of ETP-6. The NMR data from these experiments were subsequently plotted on a graph, as illustrated in the manuscript.

For the other catalysts, full titrations were not carried out. In these cases, the same molar solution as B was prepared. We prepared another NMR tube by adding 100 µL of solution A. To this tube, carefully introduced 150 µL of different catalyst solution using a microsyringe and add 250 µL of CCl_4.

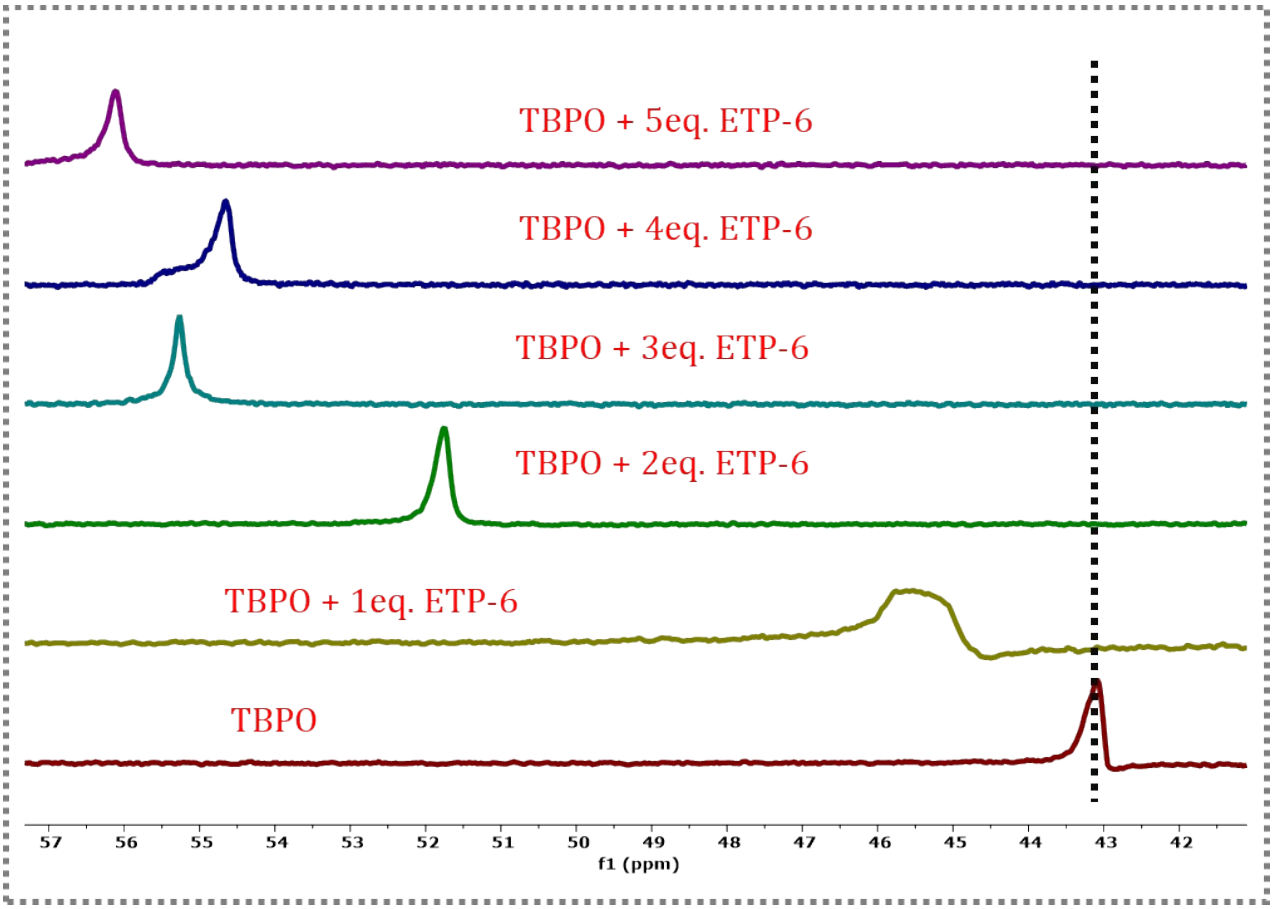
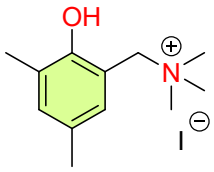


Fig. S2 NMR titration data of ETP-6 with Tributylphosphine oxide (n-Bu_3PO)

8. Characterization data of synthesised catalysts

1. 1-(2-hydroxy-3,5-dimethylphenyl)-*N*,*N*,*N*-trimethylmethanaminium iodide (ETP-1)

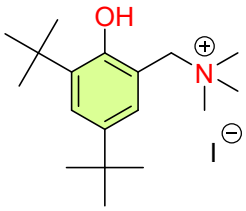


White solid, Yield : 48%

^{1}H NMR (500 MHz, DMSO) δ 8.73 (s, 1H), 7.12 (s, 3H), 4.38 (s, 3H), 3.13 (s, 6H), 2.19 (s, 9H).

^{13}C NMR (126 MHz, CDCl3) δ 154.30, 132.41, 123.82, 117.48, 66.16, 53.78, 53.74, 46.98, 15.96.

2. 1-(2-hydroxy-3,5-dimethylphenyl)-N,N,N-trimethylmethanaminium iodide (ETP-2)

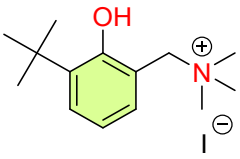


White solid, Yield : 85%

^{1}H NMR (500 MHz, DMSO) δ 8.66 (s, 1H), 7.39 (s, 1H), 7.32 (s, 1H), 4.68 (s, 2H), 3.12 (s, 6H), 2.76 (s, 3H), 1.40 (s, 9H), 1.29 (s, 9H).

^{13}C NMR (126 MHz, DMSO) δ 153.23, 142.06, 138.82, 129.55, 125.90, 116.86, 63.40, 54.39, 48.06, 34.83, 33.99, 31.28, 29.79.

3. 1-(3-(tert-butyl)-2-hydroxyphenyl)-*N*,*N*,*N*-trimethylmethanaminium iodide (ETP-3)

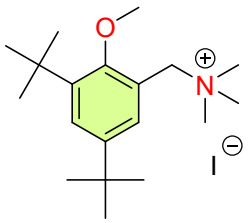


White solid, Yield : 78%

^{1}H NMR (500 MHz, DMSO) δ 8.96 (s, 1H), 7.39 (d, *J* = 9.7 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 6.96 (s, 1H), 4.64 (s, 2H), 3.02 (s, 9H), 1.38 (s, 9H).

^{13}C NMR (126 MHz, DMSO) δ 155.66, 139.25, 132.46, 129.29, 120.22, 116.85, 63.47, 54.51, 51.86, 34.71, 29.66

4. 1-(3,5-di-tert-butyl-2-methoxyphenyl)-*N*,*N*,*N*-trimethylmethanaminium iodide (ETP-4)

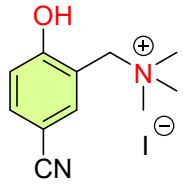


White solid, Yield : 46%

^{1}H NMR (500 MHz, DMSO) δ 7.48 (d, *J* = 2.6 Hz, 1H), 7.42 (d, *J* = 2.6 Hz, 1H), 4.51 (s, 2H), 3.78 (s, 3H), 2.97 (s, 9H), 1.38 (s, 9H), 1.30 (s, 9H).

^{13}C NMR (126 MHz, DMSO) δ 140.02, 136.23, 88.29, 73.70, 61.41, 44.50, 43.74, 9.61

5. 1-(5-cyano-2-hydroxyphenyl)-*N,N,N*-trimethylmethanaminium iodide (ETP-5)

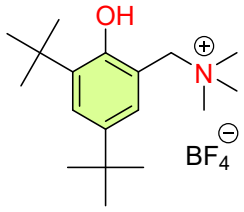


White solid, Yield: 89%

^{1}H NMR (500 MHz, DMSO) δ 11.59 (s, 1H), 7.91 (d, J = 2.2 Hz, 1H), 7.82 (dd, J = 8.5, 2.1 Hz, 1H), 7.11 (d, J = 8.6 Hz, 1H), 4.48 (s, 2H), 3.06 (s, 9H).

^{13}C NMR (126 MHz, DMSO) δ 161.57, 139.22, 136.09, 118.92, 117.29, 116.31, 101.54, 61.93, 52.28.

6. 1-(2-hydroxy-3,5-dimethylphenyl)-*N,N,N*-trimethylmethanaminium tetrafluoroborate (ETP-6)

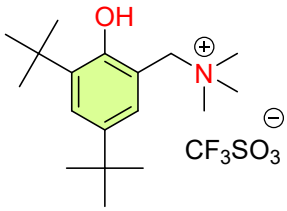


White solid, Yield: 87%

^{1}H NMR (500 MHz, CD_3CN) δ 7.72 (d, *J* = 2.5 Hz, 1H), 7.50 (d, *J* = 2.5 Hz, 1H), 6.51 (s, 1H), 4.51 (d, *J* = 5.7 Hz, 2H), 3.04 (d, *J* = 5.1 Hz, 6H), 2.36 (s, 3H), 1.68 (s, 9H), 1.56 (s, 9H).

^{13}C NMR (126 MHz, CD_3CN) δ 151.87, 145.21, 139.23, 127.86, 127.11, 120.16, 59.26, 43.52, 35.23, 34.97, 31.66, 31.50, 30.80, 30.16, 29.65.

7. 1-(3,5-di-tert-butyl-2-hydroxyphenyl)-*N,N,N*-trimethylmethanaminium trifluoromethanesulfonate (ETP-7)

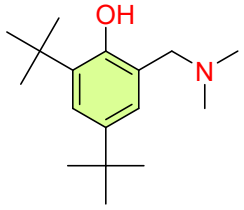


White solid, Yield : 83%

^{1}H NMR (500 MHz, CD_3CN) δ 7.50 (d, *J* = 2.5 Hz, 1H), 7.25 (d, *J* = 2.5 Hz, 1H), 6.50 (s, 1H), 4.46 (s, 2H), 2.99 (s, 9H), 1.41 (s, 9H), 1.31 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 153.33, 144.66, 139.91, 130.13, 127.96, 65.85, 53.49, 53.45, 53.42, 35.55, 34.99, 31.56, 30.21.

8. 2,4-di-tert-butyl-6-((dimethylamino)methyl)phenol (DMAMP)

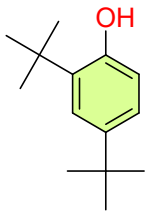


White solid, 83%

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 2.5 Hz, 1H), 6.81 (d, *J* = 2.5 Hz, 1H), 3.60 (s, 2H), 2.31 (s, 6H), 1.42 (s, 9H), 1.28 (s, 8H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.61, 140.41, 135.51, 123.24, 122.91, 121.44, 63.74, 44.45, 34.97, 34.26, 31.84, 29.74

9. 2,4-di-tert-butylphenol (DTBP)



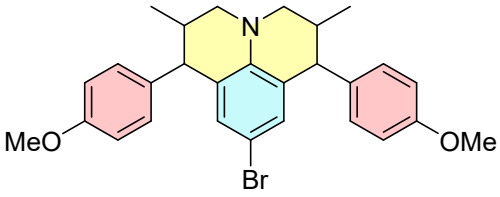
Yellowish Crystals

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (s, 1H), 7.08 (d, *J* = 8.2 Hz, 1H), 6.59 (d, *J* = 8.2 Hz, 1H), 4.61 (s, 1H), 1.42 (s, 9H), 1.29 (s, 9H).

^{13}C NMR (126 MHz, DMSO) δ 151.89, 143.12, 135.31, 124.24, 123.68, 116.06, 34.87, 34.42, 31.77, 29.81.

9. Characterization data of julolidine products (Mixture of distereomers)[3]

1. 9-bromo-1,7-bis(4-methoxyphenyl)-2,6-dimethyl-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline (4a)

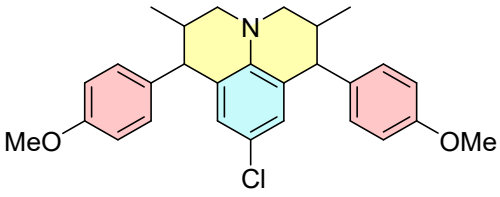


Yellow solid, Melting point: 135-136 °C

^{1}H NMR (600 MHz, CHLOROFORM-D) δ 7.08 – 6.98 (m, 4H), 6.88 – 6.82 (m, 4H), 6.46 (d, J = 46.1 Hz, 2H), 3.80 (d, J = 6.3 Hz, 6H), 3.58 (dd, J = 41.9, 8.1 Hz, 2H), 3.14 (dt, J = 11.5, 3.8 Hz, 2H), 2.92 – 2.78 (m, 2H), 2.22 (tdd, J = 9.5, 6.5, 3.5 Hz, 2H), 0.94 (dd, J = 49.5, 6.7 Hz, 6H).

^{13}C NMR (151 MHz, CHLOROFORM-D) δ 158.29, 158.19, 141.66, 140.71, 137.75, 137.22, 132.11, 130.12, 129.99, 129.90, 129.20, 128.31, 128.15, 126.64, 124.74, 120.95, 118.41, 113.96, 113.89, 56.13, 55.34, 54.04, 51.36, 50.39, 34.83, 34.03, 18.58, 18.12.

2. 9-chloro-1,7-bis(4-methoxyphenyl)-2,6-dimethyl-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline (4b)



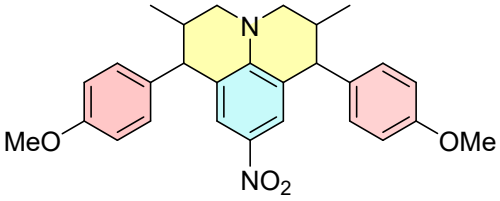
Yellow solid, Melting point: 122-124 °C

^{1}H NMR (600 MHz, CHLOROFORM-D) δ 7.10 – 6.99 (m, 4H), 6.87 (t, J = 9.4 Hz, 4H), 6.63 (d, J = 43.6 Hz, 2H), 3.81 (d, J = 6.7 Hz, 6H), 3.61 (dd, J =

39.4, 7.8 Hz, 2H), 3.15 (dd, J = 11.5, 3.6 Hz, 2H), 2.94 – 2.84 (m, 2H), 2.28 – 2.10 (m, 2H), 0.96 (dd, J = 48.3, 6.8 Hz, 6H).

^{13}C NMR (151 MHz, CHLOROFORM-D) δ 158.27, 158.17, 142.01, 141.09, 137.71, 137.19, 131.12, 130.99, 130.07, 129.86, 126.93, 125.13, 113.95, 113.88, 107.25, 55.89, 55.31, 53.92, 51.21, 50.29, 34.72, 33.95, 18.57, 18.13.

3. **1,7-bis(4-methoxyphenyl)-2,6-dimethyl-9-nitro-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline (4c)**

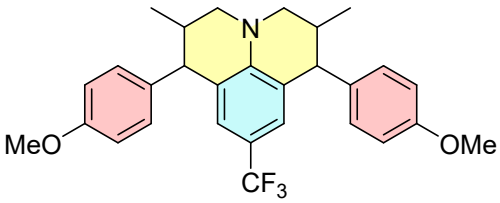


Yellow oil

^{1}H NMR (600 MHz, CHLOROFORM-D) δ 7.51 (d, J = 21.4 Hz, 2H), 7.05 – 6.99 (m, 2H), 6.96 (d, J = 8.5 Hz, 2H), 6.87 (dd, J = 11.3, 8.4 Hz, 4H), 3.78 (d, J = 6.9 Hz, 6H), 3.61 (s, 2H), 3.32 – 3.24 (m, 2H), 3.05 (dd, J = 12.5, 7.3 Hz, 2H), 2.18 (dtd, J = 18.0, 6.8, 4.0 Hz, 2H), 1.27 – 1.21 (m, 2H), 0.93 (dd, J = 25.5, 6.6 Hz, 6H).

^{13}C NMR (151 MHz, CHLOROFORM-D) δ 158.42, 158.39, 147.48, 147.15, 135.85, 135.80, 129.58, 129.49, 125.31, 125.27, 122.69, 122.07, 114.12, 55.20, 54.79, 54.17, 50.11, 49.74, 33.12, 32.78, 18.08, 17.90.

4. **1,7-bis(4-methoxyphenyl)-2,6-dimethyl-9-(trifluoromethyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline (4d)**



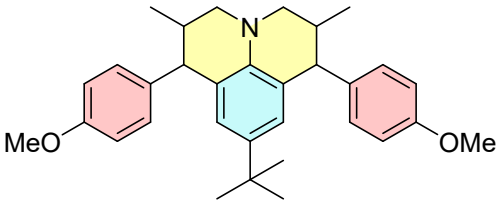
Yellow oil

^{1}H NMR (600 MHz, CHLOROFORM-D) δ 7.07 – 7.03 (m, 2H), 7.01 – 6.98 (m, 2H), 6.90 – 6.85 (m, 4H), 6.80 (d, J = 31.8 Hz, 2H), 3.80 (d, J = 7.3 Hz, 6H), 3.66 (dd, J = 32.2, 7.4 Hz, 2H), 3.22 (ddd, J = 11.5, 7.2, 3.9 Hz, 2H), 2.96 (dt, J = 12.0, 8.1 Hz,

2H), 2.20 (dddd, J = 23.3, 10.5, 7.0, 3.8 Hz, 2H), 0.97 (dd, J = 35.3, 6.7 Hz, 6H).

^{13}C NMR (151 MHz, CHLOROFORM-D) δ 158.31, 158.25, 144.92, 144.30, 137.41, 137.15, 129.94, 129.78, 125.79, 125.65, 123.43, 122.20, 114.62, 114.44, 114.00, 113.96, 55.30, 55.01, 53.79, 50.76, 50.16, 34.05, 33.49, 18.52, 18.21.

5. **9-(tert-butyl)-1,7-bis(4-methoxyphenyl)-2,6-dimethyl-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline (4e)**

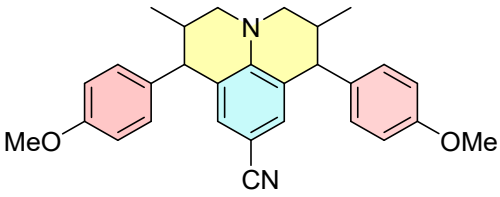


Yellow oil,

^{1}H NMR (600 MHz, CHLOROFORM-D) δ 7.03 (d, J = 8.6 Hz, 4H), 6.85 – 6.82 (m, 4H), 6.67 (d, J = 2.5 Hz, 2H), 6.61 (d, J = 8.6 Hz, 2H), 3.81 (s, 6H), 3.60 (d, J = 9.0 Hz, 2H), 3.15 (dd, J = 11.2, 3.7 Hz, 2H), 2.94 (dd, J = 11.1, 9.1 Hz, 2H), 2.18 (s, 9H), 1.60 (s, 2H), 0.91 (d, J = 6.4 Hz, 6H).

^{13}C NMR (151 MHz, CHLOROFORM-D) δ 158.04, 144.61, 139.07, 138.06, 130.23, 130.10, 127.65, 125.57, 123.80, 113.66, 113.61, 110.58, 57.16, 55.33, 51.41, 39.65, 35.50, 33.79, 31.54, 31.49, 31.05, 18.29.

6. **1,7-bis(4-methoxyphenyl)-2,6-dimethyl-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline-9-carbonitrile (4f)**



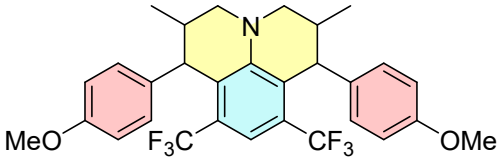
Yellow oil

^{1}H NMR (600 MHz, CHLOROFORM-D) δ 7.01 (d, J = 8.4 Hz, 2H), 6.95 (d, J = 8.4 Hz, 2H), 6.86 (t, J = 8.0 Hz, 5H), 6.73 (d, J = 17.8 Hz, 2H), 3.80 (d, J = 5.3 Hz, 6H), 3.55 (dd, J = 22.1, 8.2 Hz, 2H), 3.23 (dt, J = 12.0, 4.5 Hz, 2H), 3.06 – 2.97 (m, 2H), 1.31 – 1.22 (m, 2H), 0.91 (dd, J = 27.0, 6.7 Hz, 6H).

^{13}C NMR (151 MHz, CHLOROFORM-D) δ

158.50, 158.45, 145.66, 145.12, 136.13, 136.07, 132.43, 132.40, 129.88, 129.76, 124.16, 123.28, 114.18, 55.37, 54.44, 50.49, 49.92, 33.35, 32.89, 18.20, 18.00.

7. **1,7-bis(4-methoxyphenyl)-2,6-dimethyl-8,10-bis(trifluoromethyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline (4g)**

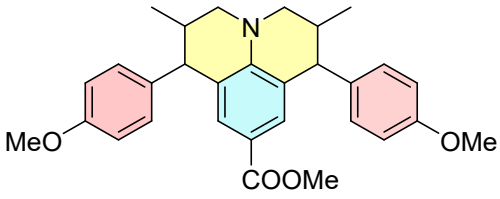


Yellow oil

^{1}H NMR (600 MHz, CHLOROFORM-D) δ 7.05 (s, 4H), 6.84 (d, J = 8.6 Hz, 4H), 6.75 (s, 1H), 3.80 (s, 2H), 3.77 (s, 6H), 3.37 (dd, J = 10.6, 5.0 Hz, 2H), 3.10 (t, J = 10.9 Hz, 2H), 2.95 – 2.79 (m, 2H), 0.98 (d, J = 6.8 Hz, 6H).

^{13}C NMR (151 MHz, CHLOROFORM-D) δ 159.40, 148.73, 148.40, 133.09, 132.87, 132.65, 132.43, 129.08, 128.98, 124.51, 124.41, 122.70, 122.60, 114.76, 114.32, 112.88, 112.17, 112.00, 111.59, 111.33, 64.98, 57.02, 55.27, 48.89, 32.29, 15.73.

8. **Methyl1,7-bis(4-methoxyphenyl)-2,6-dimethyl-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline-9-carboxylate (4h)**



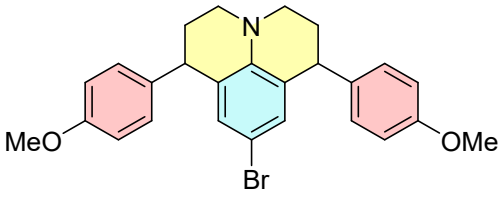
Yellow oil

^{1}H NMR (600 MHz, CHLOROFORM-D) δ 7.34 (d, J = 27.2 Hz, 2H), 7.04 (d, J = 8.5 Hz, 2H), 6.97 (d, J = 8.6 Hz, 2H), 6.85 (dd, J = 15.6, 8.6 Hz, 4H), 3.78 (d, J = 9.1 Hz, 6H), 3.73 (d, J = 6.0 Hz, 1H), 3.68 (d, J = 6.9 Hz, 1H), 3.66 (d, J = 9.0 Hz, 3H), 3.24 (ddd, J = 16.1, 12.0, 3.9 Hz, 2H), 2.97 – 2.89 (m, 2H), 2.23 – 2.12 (m, 2H), 0.98 (dd, J = 30.4, 6.9 Hz, 6H).

13C NMR (151 MHz, CHLOROFORM-D) δ

167.53, 167.47, 158.13, 158.09, 145.95, 145.52, 137.69, 137.56, 130.90, 130.78, 129.70, 129.55, 122.10, 121.24, 113.88, 113.84, 55.20, 54.26, 53.41, 51.16, 50.21, 49.80, 33.81, 33.35, 18.53, 18.27.

9. 9-bromo-1,7-bis(4-methoxyphenyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline (4′i)

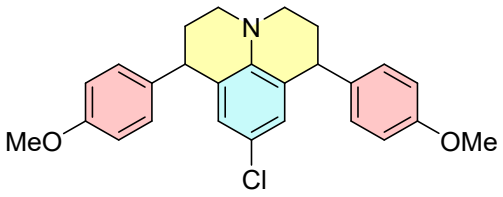


White solid, Melting point: 91-92 °C

^{1}H NMR (600 MHz, CHLOROFORM-D) δ 7.06 – 7.01 (m, 4H), 6.87 – 6.82 (m, 4H), 6.70 (s, 2H), 4.03 (dt, J = 11.3, 6.0 Hz, 2H), 3.77 (d, J = 6.5 Hz, 6H), 3.10 (qt, J = 11.9, 5.5 Hz, 4H), 2.18 (ddt, J = 13.0, 9.2, 4.8 Hz, 2H), 2.03 (ddt, J = 13.0, 6.8, 3.3 Hz, 2H).

^{13}C NMR (151 MHz, CHLOROFORM-D) δ 158.26, 138.19, 130.87, 130.84, 129.61, 126.07, 114.02, 113.99, 107.49, 107.38, 55.38, 47.34, 47.27, 42.71, 42.66, 30.61.

10. 9-chloro-1,7-bis(4-methoxyphenyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline (4′j)

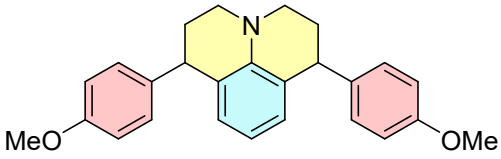


White solid, Melting point: 93-94 °C

^{1}H NMR (600 MHz, DMSO-D6) δ 7.12 – 7.02 (m, 4H), 6.85 (dd, J = 12.5, 8.0 Hz, 4H), 6.57 (s, 2H), 4.05 (dd, J = 11.6, 5.8 Hz, 2H), 3.79 (t, J = 8.7 Hz, 6H), 3.24 – 3.04 (m, 4H), 2.26 – 2.17 (m, 2H), 2.07 (dd, J = 10.5, 5.2 Hz, 2H).

^{13}C NMR (151 MHz, DMSO-D6) δ 158.00, 141.54, 138.01, 129.36, 127.80, 125.44, 125.39, 120.04, 119.95, 113.76, 113.72, 55.15, 47.21, 47.12, 42.51, 30.45.

11. 1,7-bis(4-methoxyphenyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline (4′k)

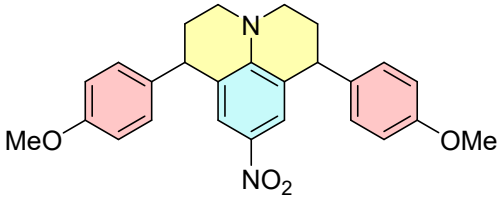


Yellow oil

^{1}H NMR (600 MHz, CHLOROFORM-D) δ 6.90 (t, J = 7.9 Hz, 4H), 6.68 (dd, J = 12.3, 8.3 Hz, 4H), 6.44 (dd, J = 7.5, 5.1 Hz, 2H), 6.22 (q, J = 7.1 Hz, 1H), 3.94 (q, J = 6.5 Hz, 2H), 3.61 (t, J = 5.8 Hz, 6H), 2.96 (ddd, J = 18.0, 7.6, 4.0 Hz, 4H), 2.16 – 2.00 (m, 2H), 1.91 (dp, J = 10.1, 3.3 Hz, 2H).

^{13}C NMR (151 MHz, CHLOROFORM-D) δ 158.02, 149.33, 143.25, 143.22, 139.23, 139.16, 129.68, 129.66, 129.40, 129.29, 129.11, 128.56, 128.53, 128.50, 127.84, 124.90, 123.96, 123.92, 120.07, 118.93, 117.29, 116.74, 115.76, 115.62, 115.15, 114.02, 113.81, 113.78, 55.36, 55.34, 47.51, 47.46, 42.82, 42.72, 30.95, 30.89.

12. 1,7-bis(4-methoxyphenyl)-9-nitro-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline (4′l)

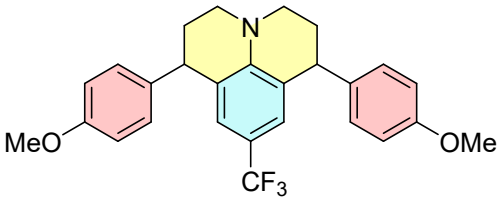


Yellow solid, Melting point: 135-136 °C

^{1}H NMR (600 MHz, CHLOROFORM-D) δ 8.22 (d, J = 3.8 Hz, 2H), 7.64 (dt, J = 16.0, 9.2 Hz, 4H), 7.59 – 7.44 (m, 4H), 4.73 (ddt, J = 19.7, 13.5, 6.3 Hz, 2H), 4.42 (s, 6H), 4.04 – 3.78 (m, 4H), 2.93 – 2.68 (m, 4H).

^{13}C NMR (151 MHz, CHLOROFORM-D) δ 158.51, 147.99, 136.40, 135.95, 129.28, 125.04, 124.95, 122.85, 122.81, 114.24, 55.41, 47.45, 47.29, 42.31, 29.28.

13. 1,7-bis(4-methoxyphenyl)-9-(trifluoromethyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline (4′m)

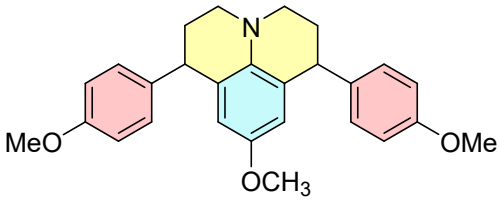


Yellow oil

^{1}H NMR (600 MHz, CHLOROFORM-D) δ 7.06 (ddd, J = 10.5, 8.6, 1.6 Hz, 4H), 6.94 – 6.85 (m, 6H), 4.13 (dt, J = 12.8, 5.7 Hz, 2H), 3.82 (dd, J = 7.6, 1.3 Hz, 6H), 3.20 (dqt, J = 20.0, 8.4, 4.5 Hz, 4H), 2.28 – 2.16 (m, 2H), 2.10 (dqd, J = 13.0, 4.5, 2.4 Hz, 2H).

^{13}C NMR (151 MHz, CHLOROFORM-D) δ 158.28, 137.82, 137.67, 129.48, 129.46, 125.42, 125.39, 125.36, 125.33, 123.06, 114.03, 114.00, 55.36, 55.35, 46.93, 46.88, 42.58, 42.47, 29.96, 29.92.

14. 9-methoxy-1,7-bis(4-methoxyphenyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline (4′n)

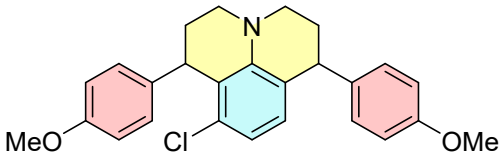


Yellow oil

^{1}H NMR (600 MHz, CHLOROFORM-D) δ 7.80 – 7.70 (m, 4H), 7.51 (dddd, J = 19.6, 8.6, 6.1, 2.2 Hz, 4H), 7.31 (t, J = 3.8 Hz, 2H), 4.55 – 4.39 (m, 6H), 3.83 – 3.63 (m, 4H), 2.99 – 2.85 (m, 2H), 2.79 – 2.63 (m, 2H), 1.95 (d, J = 2.5 Hz, 3H).

^{13}C NMR (151 MHz, CHLOROFORM-D) δ 158.55, 141.76, 141.68, 140.66, 140.25, 140.09, 138.96, 138.78, 130.33, 130.30, 126.29, 126.21, 123.88, 123.68, 117.00, 114.34, 114.31, 55.97, 48.08, 47.85, 43.67, 43.47, 34.37, 32.23, 32.18, 32.14, 32.03, 31.83.

15. 8-chloro-1,7-bis(4-methoxyphenyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline (4′o)

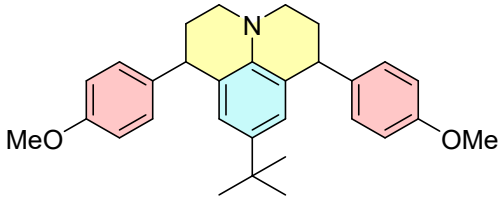


Yellow oil

^{1}H NMR (600 MHz, CHLOROFORM-D) δ 7.32 – 7.12 (m, 4H), 7.12 – 6.97 (m, 4H), 6.78 (ddd, J = 11.1, 8.2, 3.4 Hz, 1H), 6.70 (dt, J = 20.1, 5.3 Hz, 1H), 4.09 – 3.91 (m, 6H), 3.55 – 3.07 (m, 4H), 2.54 – 2.09 (m, 4H).

^{13}C NMR (151 MHz, CHLOROFORM-D) δ 158.18, 158.10, 157.89, 144.07, 144.00, 138.81, 137.88, 137.60, 133.30, 133.25, 129.58, 129.44, 129.18, 129.10, 127.49, 122.43, 121.78, 119.47, 119.34, 116.24, 115.98, 113.93, 113.84, 113.73, 113.66, 55.34, 55.31, 55.26, 55.24, 47.84, 46.40, 44.81, 44.77, 43.12, 42.03, 39.41, 39.37, 30.70, 29.88, 29.15, 29.12.

16. 9-(tert-butyl)-1,7-bis(4-methoxyphenyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline (4′p)



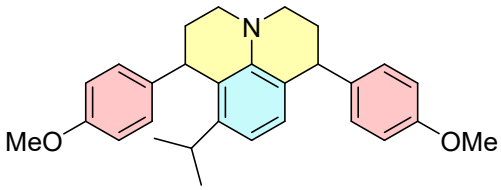
Yellow oil

^{1}H NMR (600 MHz, CHLOROFORM-D) δ 7.16 – 7.02 (m, 5H), 6.93 – 6.81 (m, 5H), 6.29 (dd, J = 80.3, 3.3 Hz, 2H), 3.83 – 3.77 (m, 6H), 3.63 (d, J = 1.5 Hz, 2H), 3.49 (d, J = 1.5 Hz, 2H), 3.16 – 3.05 (m, 4H), 2.92 – 2.87 (m, 2H), 2.32 – 2.20 (m, 2H), 2.09 (ddd, J = 18.5, 9.4, 5.2 Hz, 2H), 1.51 – 1.08 (m, 9H).

^{13}C NMR (151 MHz, CHLOROFORM-D) δ 158.72, 152.01, 142.49, 139.89, 138.87, 130.36, 130.33, 127.76, 126.40, 116.76, 115.16, 115.09, 114.46, 114.43, 113.64, 113.21, 56.43, 56.00, 49.82, 48.68, 48.57, 43.79, 43.70, 40.77, 32.48, 32.29, 30.45.

17. 8-isopropyl-1,7-bis(4-methoxyphenyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-

ij]quinoline (4′q)

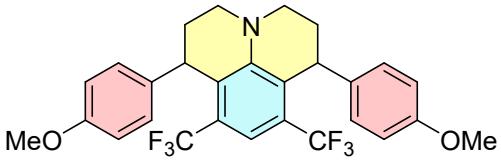


Yellow oil

^{1}H NMR (600 MHz, CHLOROFORM-D) δ 6.99 – 6.87 (m, 2H), 6.82 (dt, J = 16.4, 9.0 Hz, 2H), 6.78 – 6.55 (m, 6H), 6.55 – 6.23 (m, 2H), 4.08 – 3.85 (m, 1H), 3.60 (dt, J = 14.1, 5.9 Hz, 6H), 3.14 – 2.61 (m, 5H), 2.26 – 2.03 (m, 2H), 2.03 – 1.90 (m, 1H), 1.87 – 1.71 (m, 1H), 1.08 (dt, J = 18.7, 7.2 Hz, 6H).

^{13}C NMR (151 MHz, CHLOROFORM-D) δ 157.86, 157.76, 157.61, 149.78, 145.89, 142.56, 142.46, 139.45, 139.28, 139.11, 138.76, 138.50, 129.56, 129.50, 129.45, 129.29, 129.25, 128.99, 128.45, 128.33, 125.15, 121.26, 120.76, 119.20, 118.97, 118.17, 117.82, 115.21, 114.84, 114.17, 113.89, 113.63, 113.62, 113.54, 113.39, 113.34, 112.83, 112.66, 66.70, 66.54, 55.16, 55.13, 55.08, 51.89, 49.38, 48.57, 46.78, 44.99, 44.65, 44.60, 43.49, 42.35, 42.17, 41.51, 38.00, 37.81, 37.70, 34.36, 31.52, 31.11, 30.12, 29.88, 29.80, 29.74, 28.30, 28.25, 26.87, 24.64, 24.44, 24.30, 24.06, 23.99, 23.40, 23.14, 22.85, 22.59, 14.06.

18. 1,7-bis(4-methoxyphenyl)-8,10-bis(trifluoromethyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline (4′r)



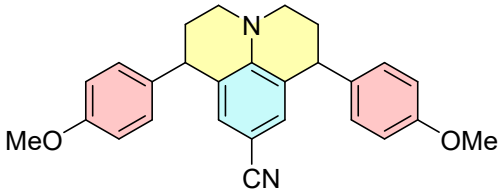
White solid, Melting point: 125-126^{o}C

^{1}H NMR (600 MHz, CHLOROFORM-D) δ 6.92 (d, J = 8.1 Hz, 5H), 6.83 (d, J = 8.2 Hz, 4H), 4.64 (s, 2H), 3.78 (s, 6H), 3.09 – 3.02 (m, 2H), 2.92 (td, J = 11.6, 6.5 Hz, 2H), 2.14 (dt, J = 8.7, 4.2 Hz, 4H).

^{13}C NMR (151 MHz, CHLOROFORM-D) δ 158.11, 143.99, 135.17, 128.63, 128.46, 127.21, 124.84, 114.66, 113.88, 113.80, 55.23, 44.75,

38.01, 28.34.

19. 1,7-bis(4-methoxyphenyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline-9-carbonitrile (4′s)

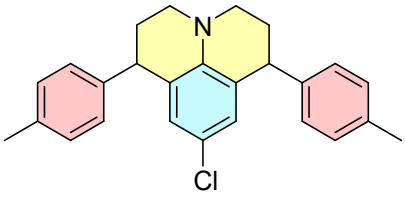


Yellow oil

^{1}H NMR (600 MHz, CHLOROFORM-D) δ 7.01 (dd, J = 12.6, 9.1 Hz, 4H), 6.91 – 6.82 (m, 6H), 4.02 (dt, J = 11.3, 5.7 Hz, 2H), 3.80 (s, 6H), 3.31 – 3.15 (m, 4H), 2.22 – 2.04 (m, 4H).

^{13}C NMR (151 MHz, CHLOROFORM-D) δ 158.45, 145.86, 136.74, 132.61, 132.05, 132.02, 129.37, 123.86, 121.16, 120.81, 119.90, 114.16, 96.15, 55.40, 47.43, 47.39, 42.30, 29.43.

20. 9-chloro-1,7-di-p-tolyl-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline (4′t)

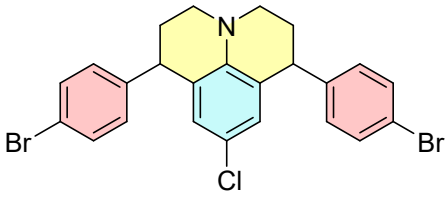


Yellow oil

^{1}H NMR (600 MHz, CHLOROFORM-D) δ 7.17 (dd, J = 12.8, 7.7 Hz, 4H), 7.07 (dd, J = 11.0, 7.8 Hz, 4H), 6.62 (s, 2H), 4.11 (dt, J = 11.7, 6.1 Hz, 2H), 3.16 (ddt, J = 12.1, 7.5, 4.0 Hz, 4H), 2.38 (d, J = 6.3 Hz, 6H), 2.27 (ddt, J = 12.9, 9.5, 4.8 Hz, 2H), 2.11 (ddq, J = 13.6, 7.1, 3.7 Hz, 2H).

^{13}C NMR (151 MHz, CHLOROFORM-D) δ 143.20, 135.96, 129.28, 129.26, 128.58, 128.10, 128.05, 125.46, 47.35, 43.18, 30.66, 21.15.

21. 1,7-bis(4-bromophenyl)-9-chloro-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline (4′u)

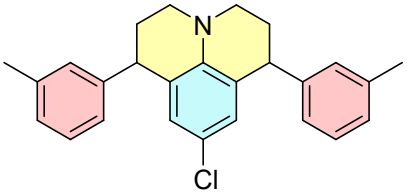


Yellow oil

^{1}H NMR (600 MHz, CHLOROFORM-*D*) δ 7.44 (dd, *J* = 14.6, 8.2 Hz, 4H), 7.01 (dd, *J* = 14.3, 8.1 Hz, 4H), 6.55 (d, *J* = 10.5 Hz, 2H), 4.07 (dt, *J* = 16.5, 6.2 Hz, 2H), 3.22 – 3.01 (m, 4H), 2.23 (ddd, *J* = 13.3, 8.4, 4.2 Hz, 2H), 2.04 (ddq, *J* = 13.0, 6.5, 2.9 Hz, 2H).

^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 145.02, 144.94, 141.69, 131.71, 131.66, 130.36, 130.34, 128.30, 128.19, 124.80, 124.65, 120.38, 120.33, 47.33, 46.98, 42.95, 30.37.

22. 9-chloro-1,7-di-m-tolyl-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline (4′v)



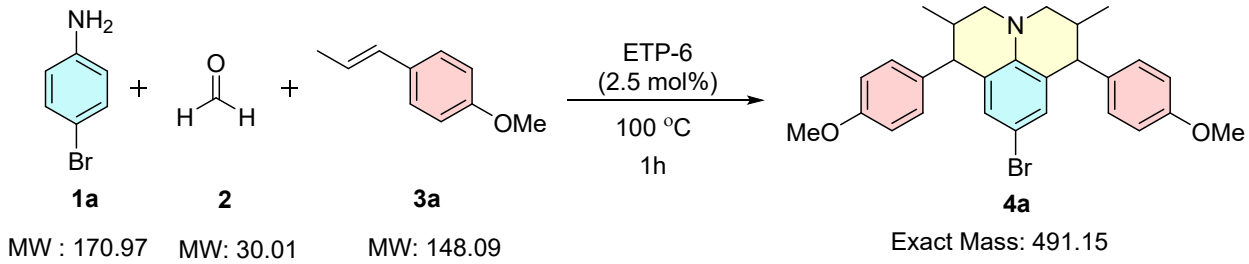
Yellow oil

^{1}H NMR (600 MHz, CHLOROFORM-*D*) δ 7.27 – 7.22 (m, 2H), 7.10 (dd, *J* = 7.5, 4.9 Hz, 2H), 7.04 – 6.95 (m, 4H), 6.65 (d, *J* = 6.8 Hz, 2H), 4.13 (dt, *J* = 10.5, 6.2 Hz, 2H), 3.32 – 3.08 (m, 4H), 2.40 (d, *J* = 10.2 Hz, 6H), 2.29 (ddd, *J* = 12.6, 8.5, 3.2 Hz, 2H), 2.14 (dtd, *J* = 13.2, 6.7, 4.2 Hz, 2H).

^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 146.19, 141.92, 138.14, 138.09, 129.47, 129.41, 128.46, 128.19, 128.15, 127.29, 125.92, 125.84, 125.44, 120.30, 119.13, 112.17, 47.46, 47.42, 43.59, 43.53, 30.68, 30.52, 21.71, 21.66.

10. Green metrics calculation:

Green matrix such as Atom Economy (AE), Atom Efficiency (AEf), Reaction Mass Efficiency (RME), Optimum Efficiency (OE) have been calculated for the following reaction:



1a MW : 170.97 **2** MW: 30.01 **3a** MW: 148.09 **4a** Exact Mass: 491.15

The vial containing a mixture of 4-bromo aniline **1a** (1.0 mmol), paraformaldehyde **2** (3.0 mmol), *trans*-anethole **3a** (3.0 mmol), and ETP-6 (2.5 mol %) was sealed and placed at 100 °C under stirring for 1 h. Afterward, the reaction mixture was cooled to room temperature make a slurry in 100-200 mess silica. The obtained solid was purified by silica gel column chromatography (hexane/ dichloromethane/ethyl acetate) to afford the julolidines in high purities. All products were characterized by ^{1}H and ^{13}C NMR. Isolated yield is 86.20%.

Materials used for metrics calculations: 4-Bromo aniline (1 mmol, 107.15 mg), paraformaldehyde (3 mmol, 90 mg), ETP-6 (2.5 mol%, 9 mg), *trans*-anethole (3 mmol, 444.27 mg), compound **4a** (0.862 mmol, 423.37 mg).

Green matrix	**Formula**[4]	**Calculation**
Atom Economy **(AE)**	$\frac{\text{MW of product}}{\text{Total MW of reactants}} \times 100$	$\frac{491.15}{170.97+90+444.27} \times 100 =$ **69.64**
Atom Efficiency **(AEf)**	$\frac{\text{AE}}{100} \times \text{yield\%}$	$\frac{69.64}{100} \times 86.20 =$ **60.029**
Reaction Mass Efficiency **(RME)**	$\frac{\text{Mass of isolated product}}{\text{Total mass of reactants}} \times 100$	$\frac{423.37}{170.97+90+444.27} \times 100 =$ **60.13**
Optimum Efficiency **(OE)**	$\frac{\text{RME}}{\text{AE}} \times 100$	$\frac{60.13}{69.64} \times 100 =$ **86.34**

11. ^{1}H and ^{13}C NMR of Catalyst

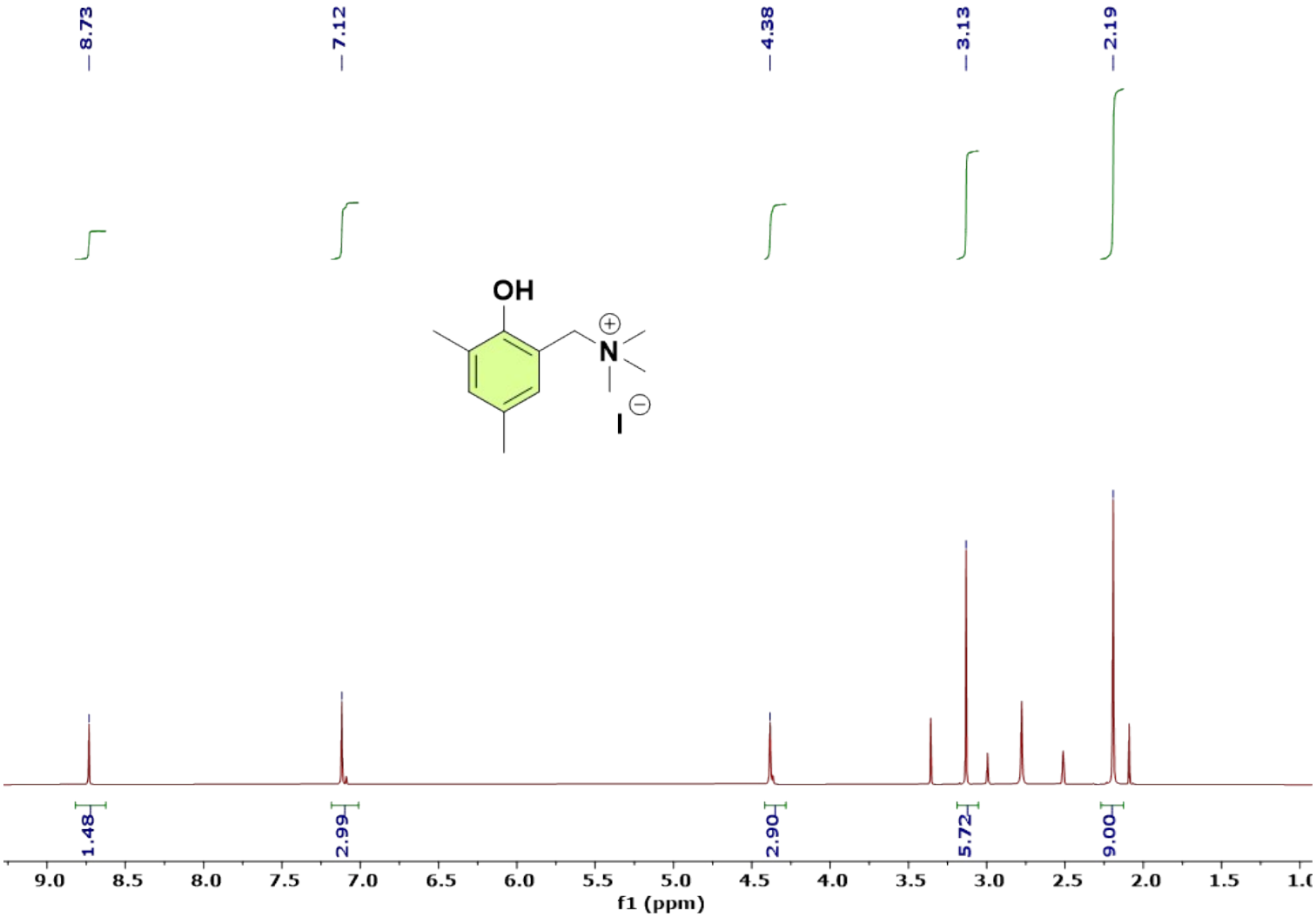


Fig. S3 ^{1}H NMR Spectrum of ETP-1 (DMSO, 500 MHz, 298K)

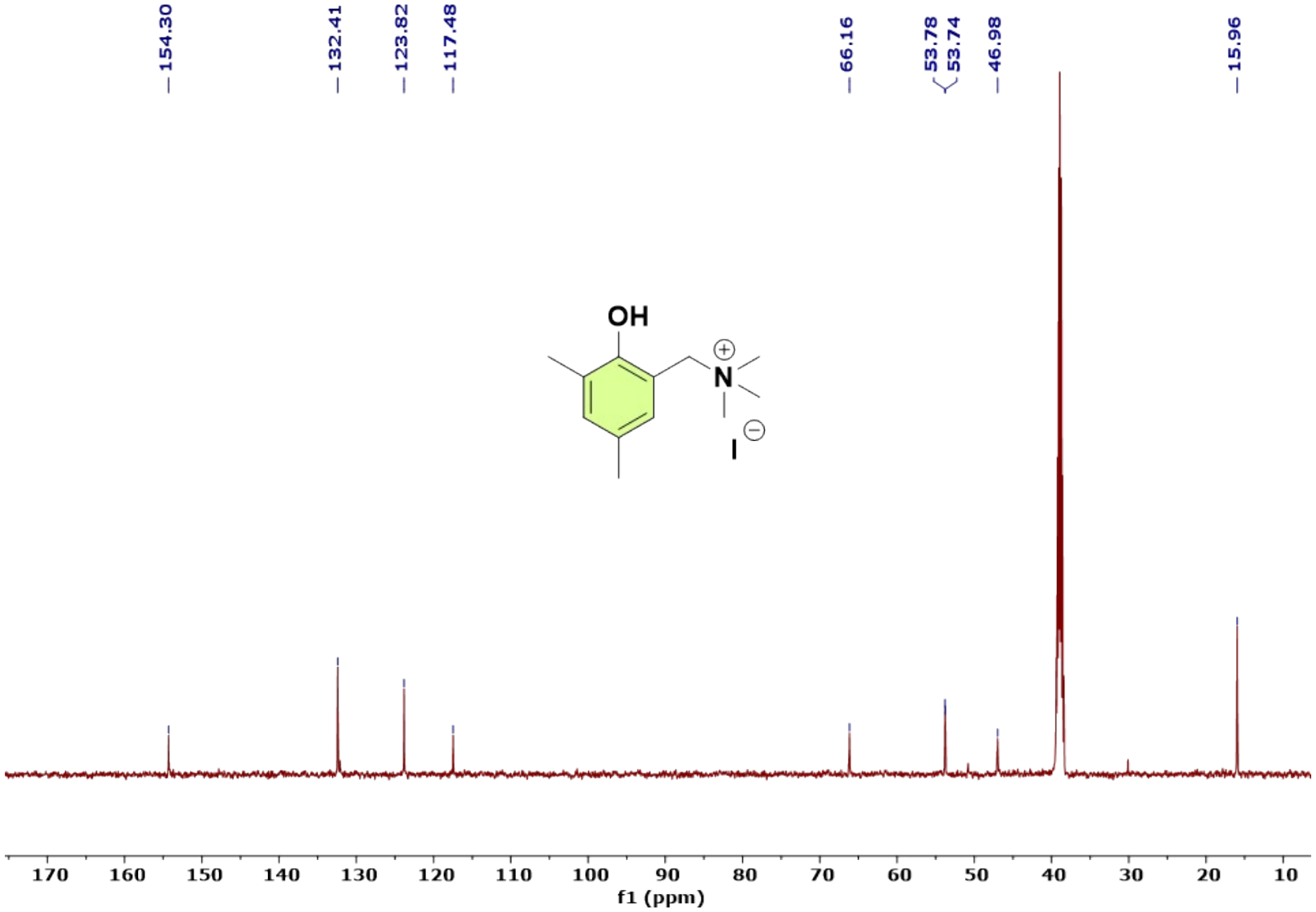


Fig. S4 ^{13}C NMR Spectrum of ETP-1 (DMSO, 126 MHz, 298K)

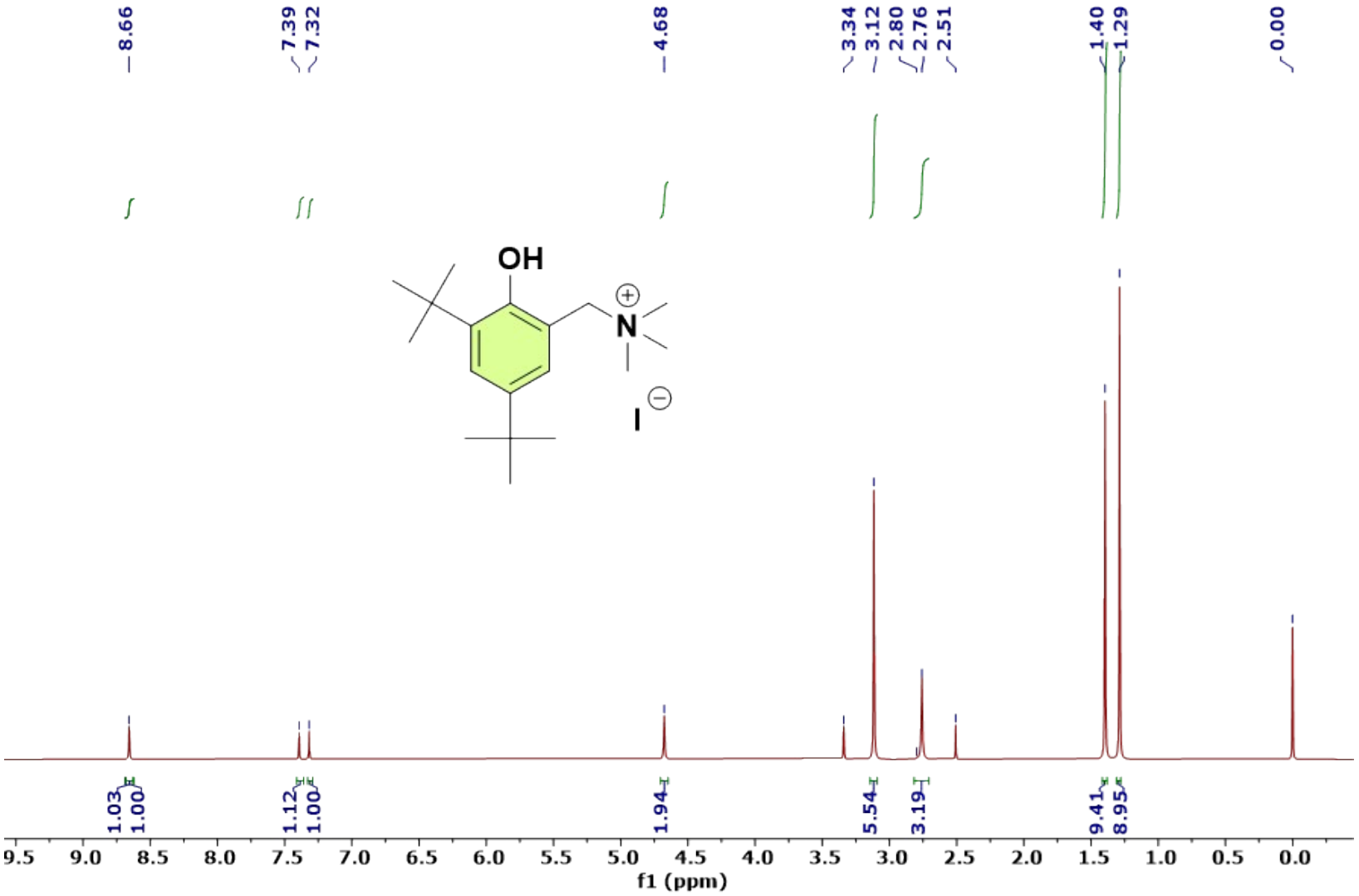


Fig. S5 ^{1}H NMR Spectrum of ETP-2 (DMSO, 500 MHz, 298K)

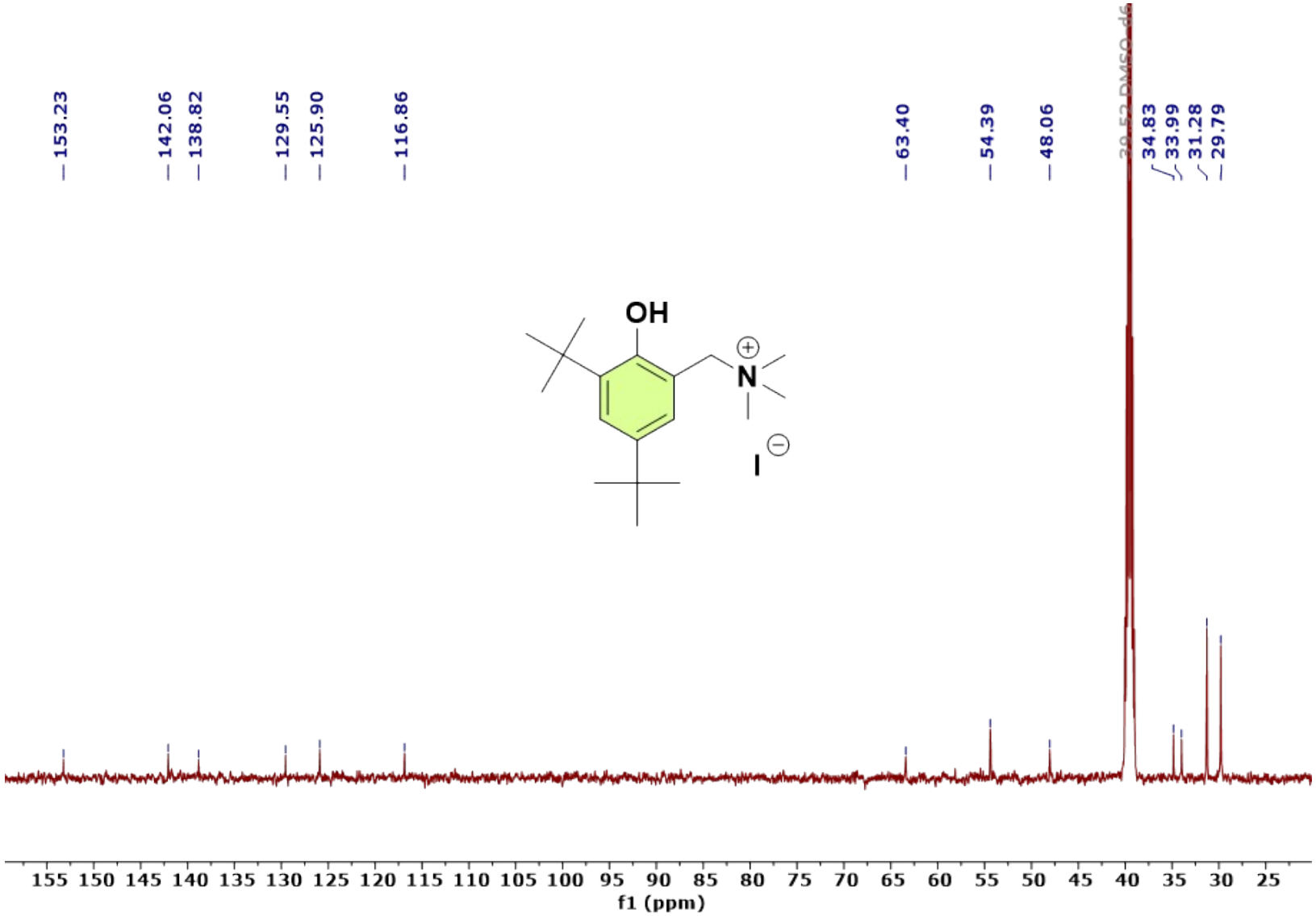


Fig. S6 ^{13}C NMR Spectrum of ETP-2 (DMSO, 126 MHz, 298K)

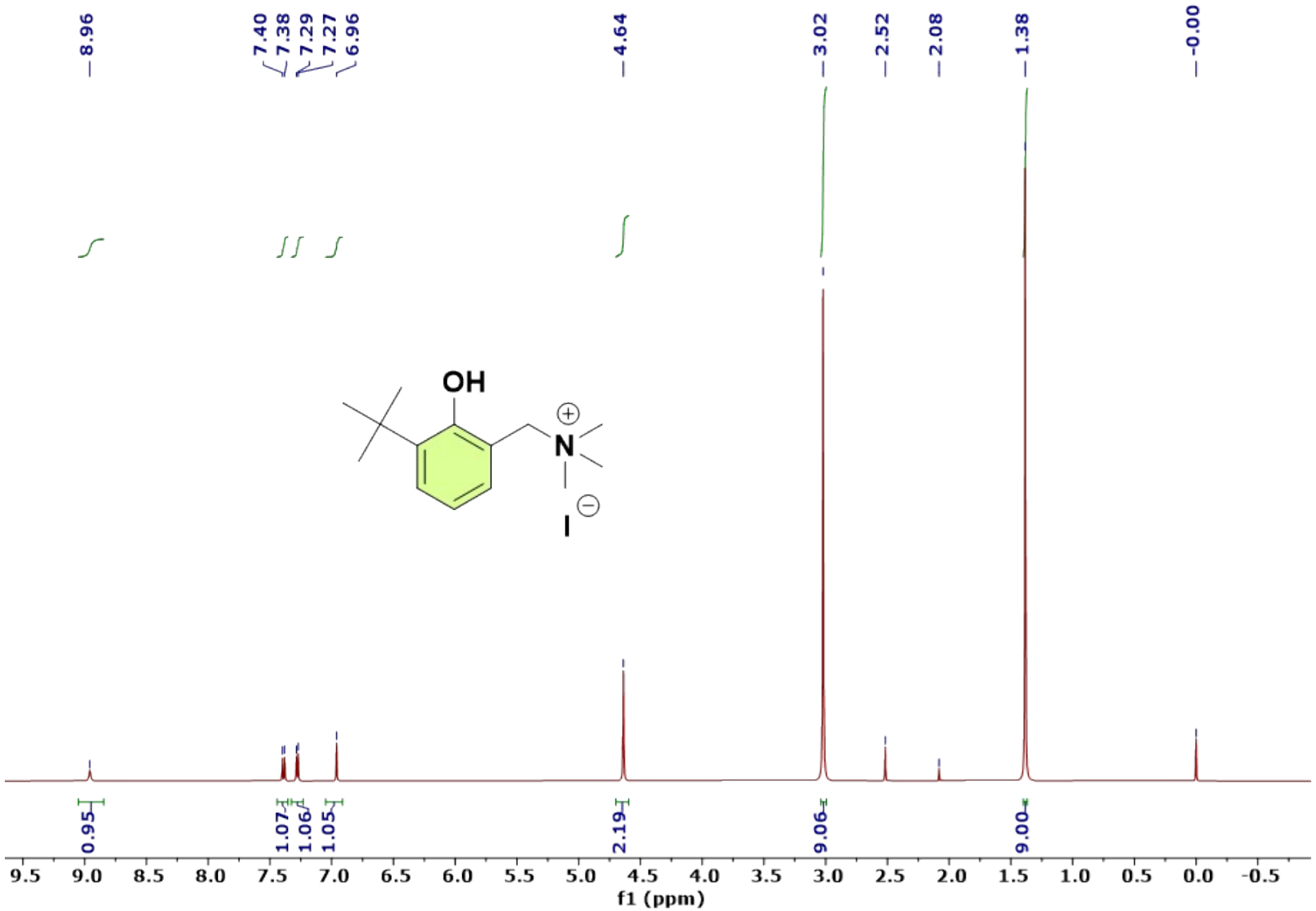


Fig. S7 ^{1}H NMR Spectrum of ETP-3 (DMSO, 500 MHz, 298K)

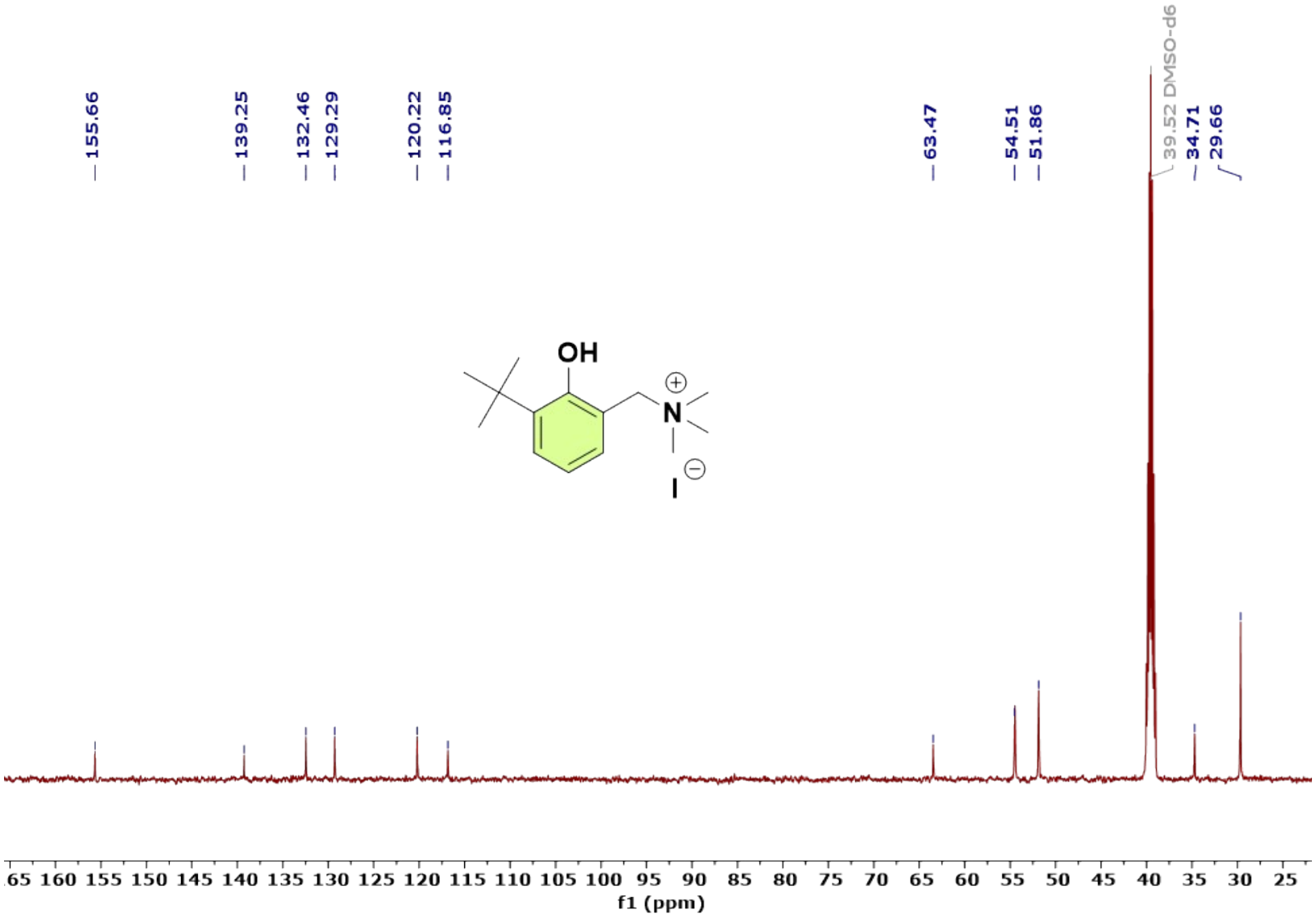


Fig. S8 ^{13}C NMR Spectrum of ETP-3 (DMSO, 126 MHz, 298K)

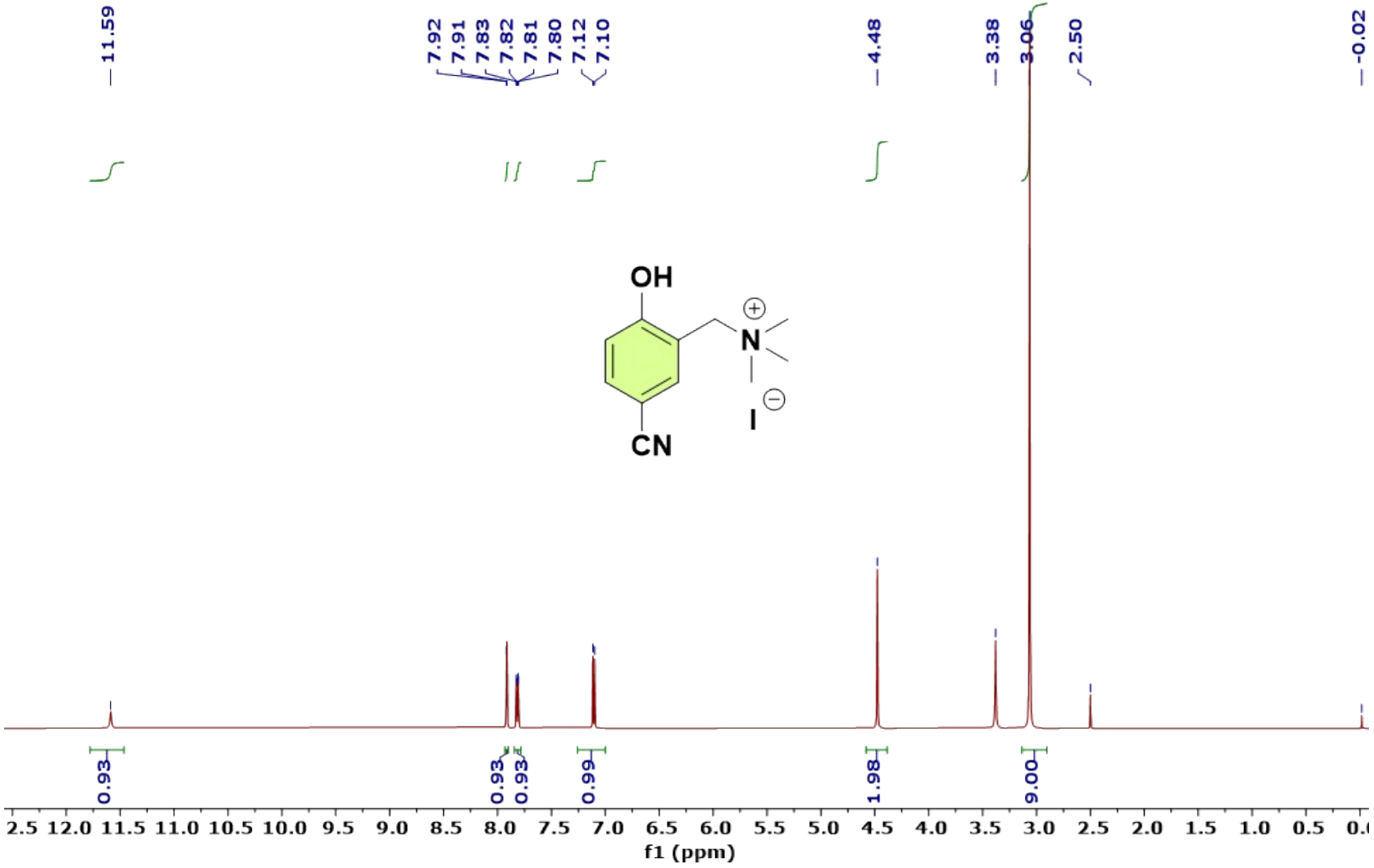


Fig. S9 ^{1}H NMR Spectrum of ETP-4 (DMSO, 500 MHz, 298K)

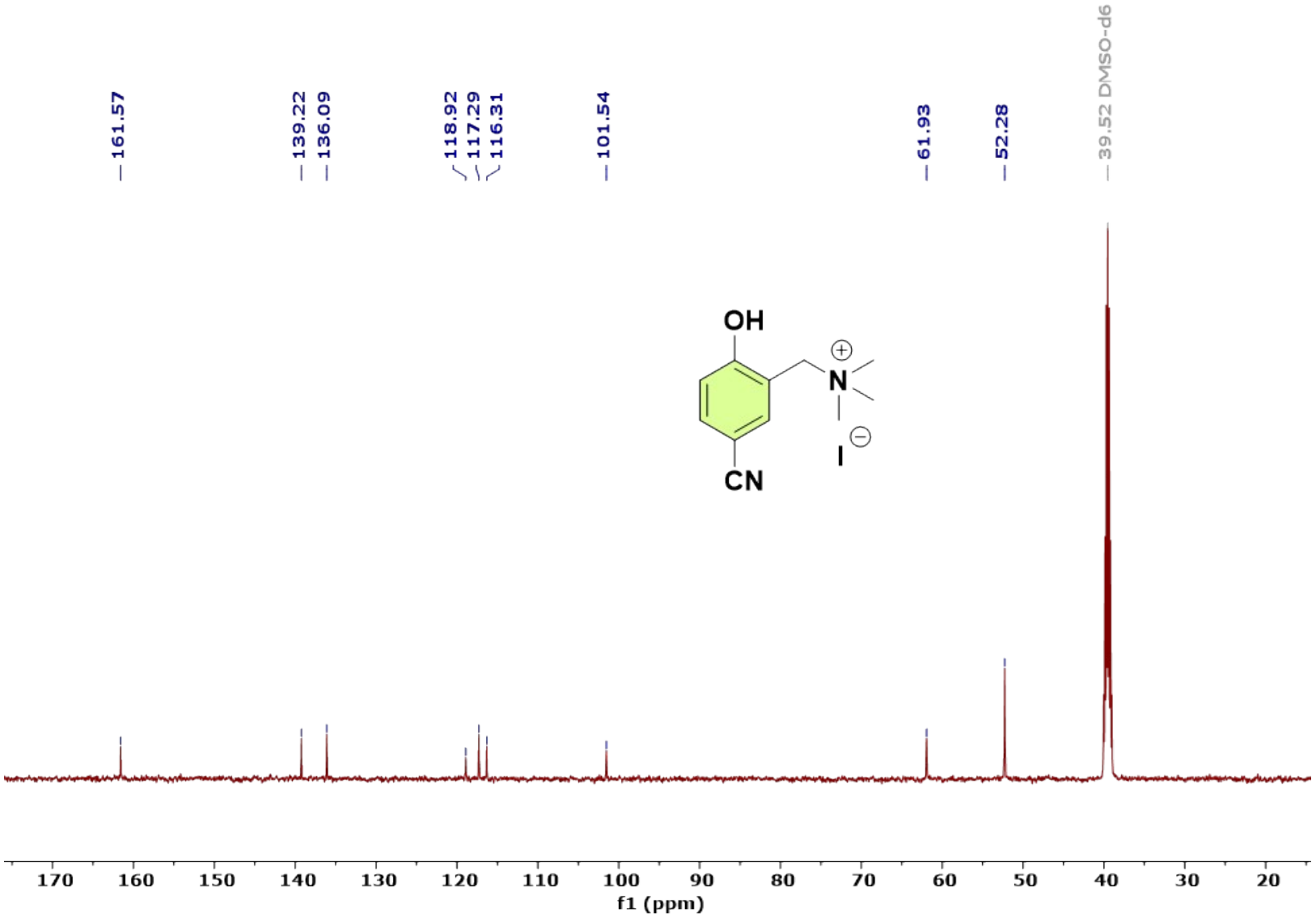


Fig. S10 ^{13}C NMR Spectrum of ETP-4 (DMSO, 126 MHz, 298K)

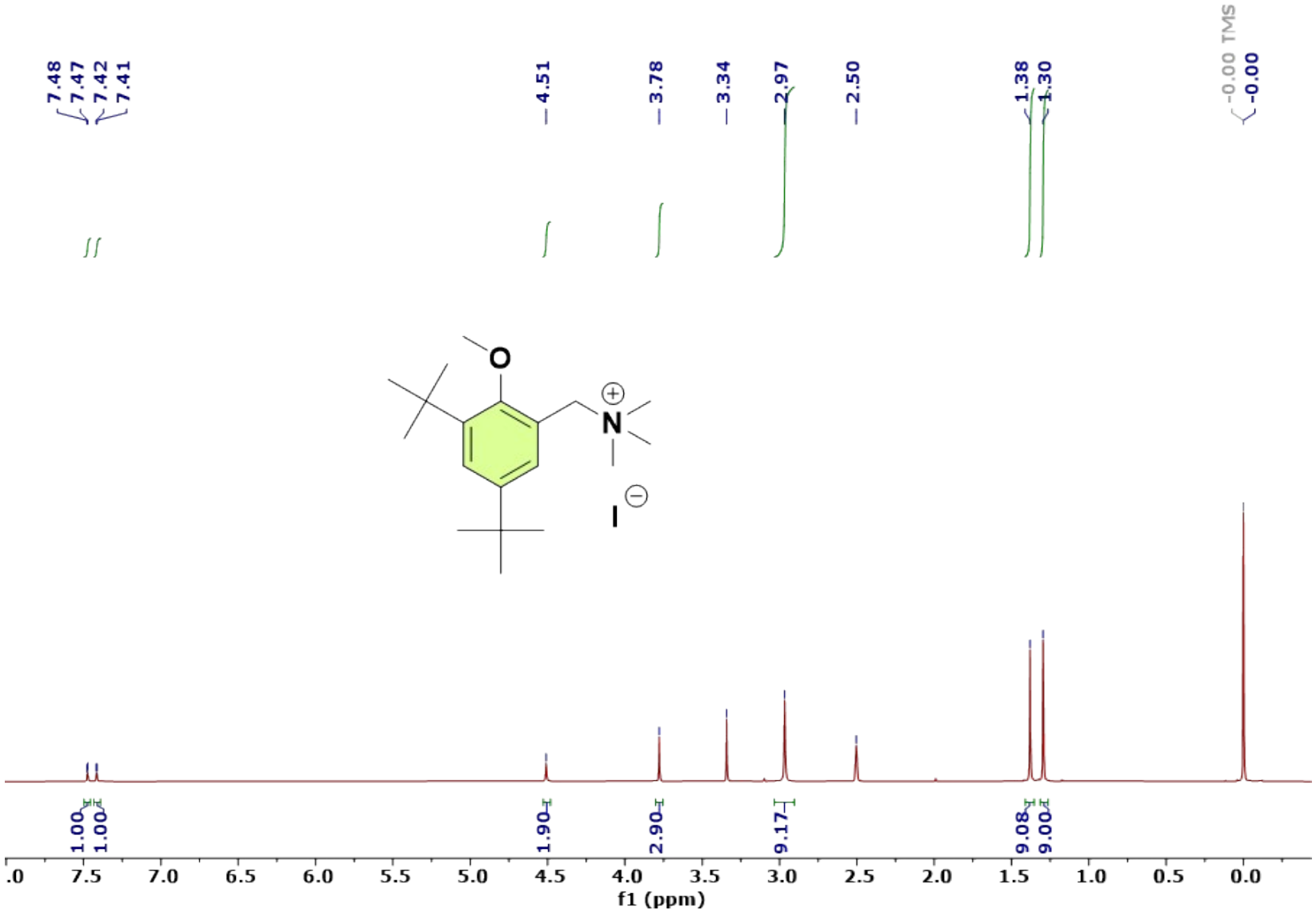


Fig. S11 ^{1}H NMR Spectrum of ETP-5 (DMSO, 500 MHz, 298K)

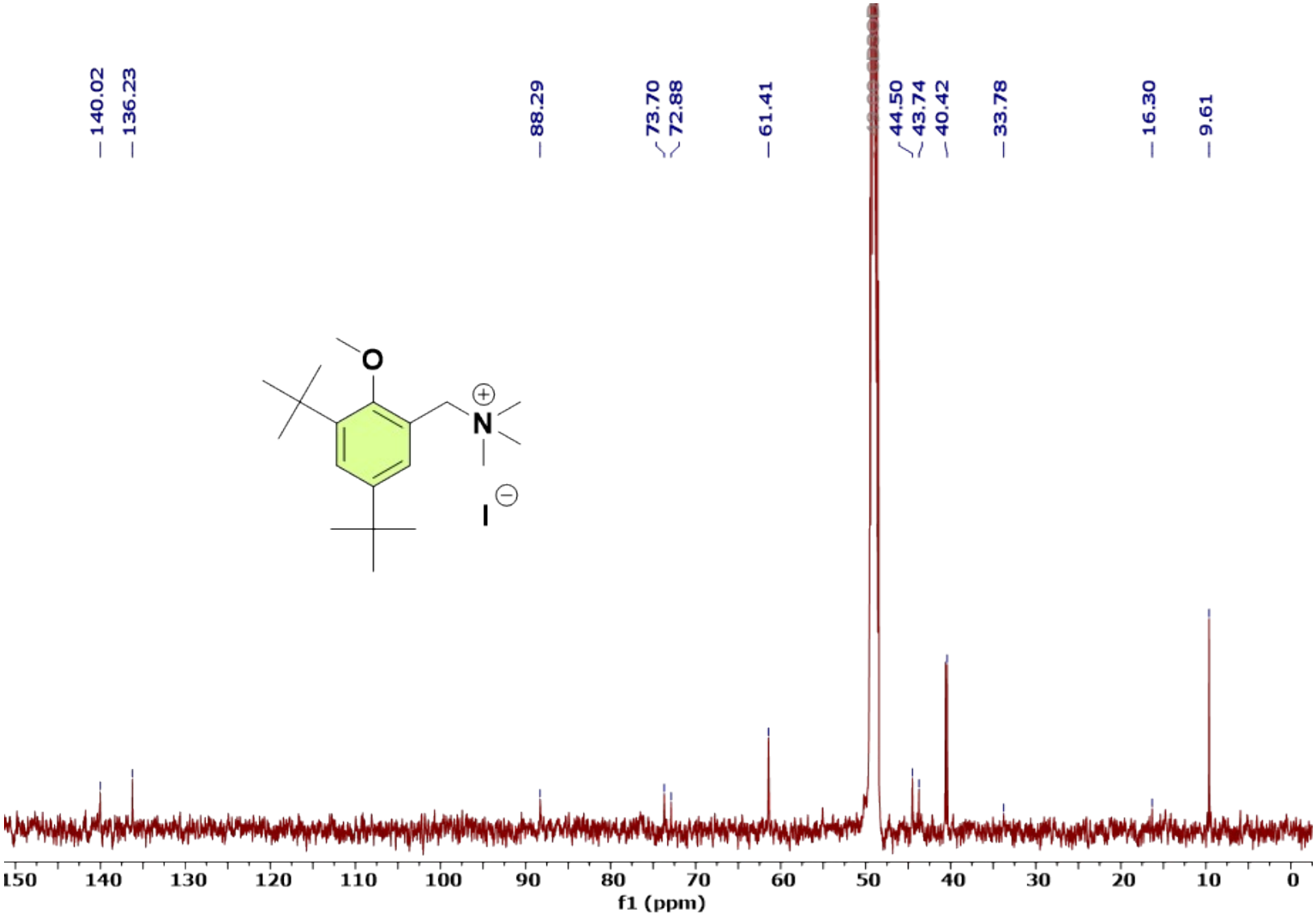


Fig. S12 ^{13}C NMR Spectrum of ETP-5(DMSO, 126 MHz, 298K)

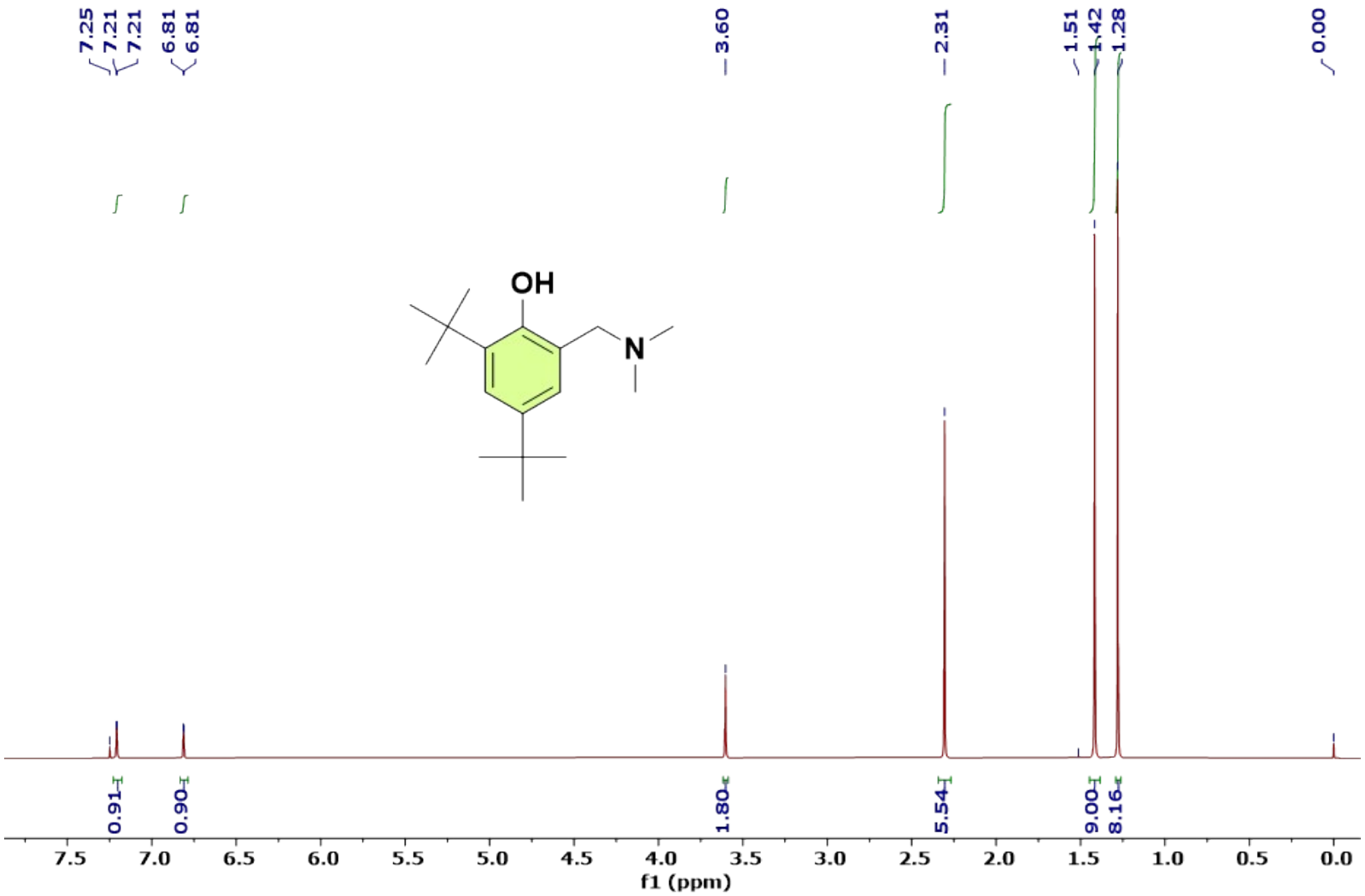


Fig. S13 ^{1}H NMR Spectrum of DMAMP (DMSO, 500 MHz, 298K)

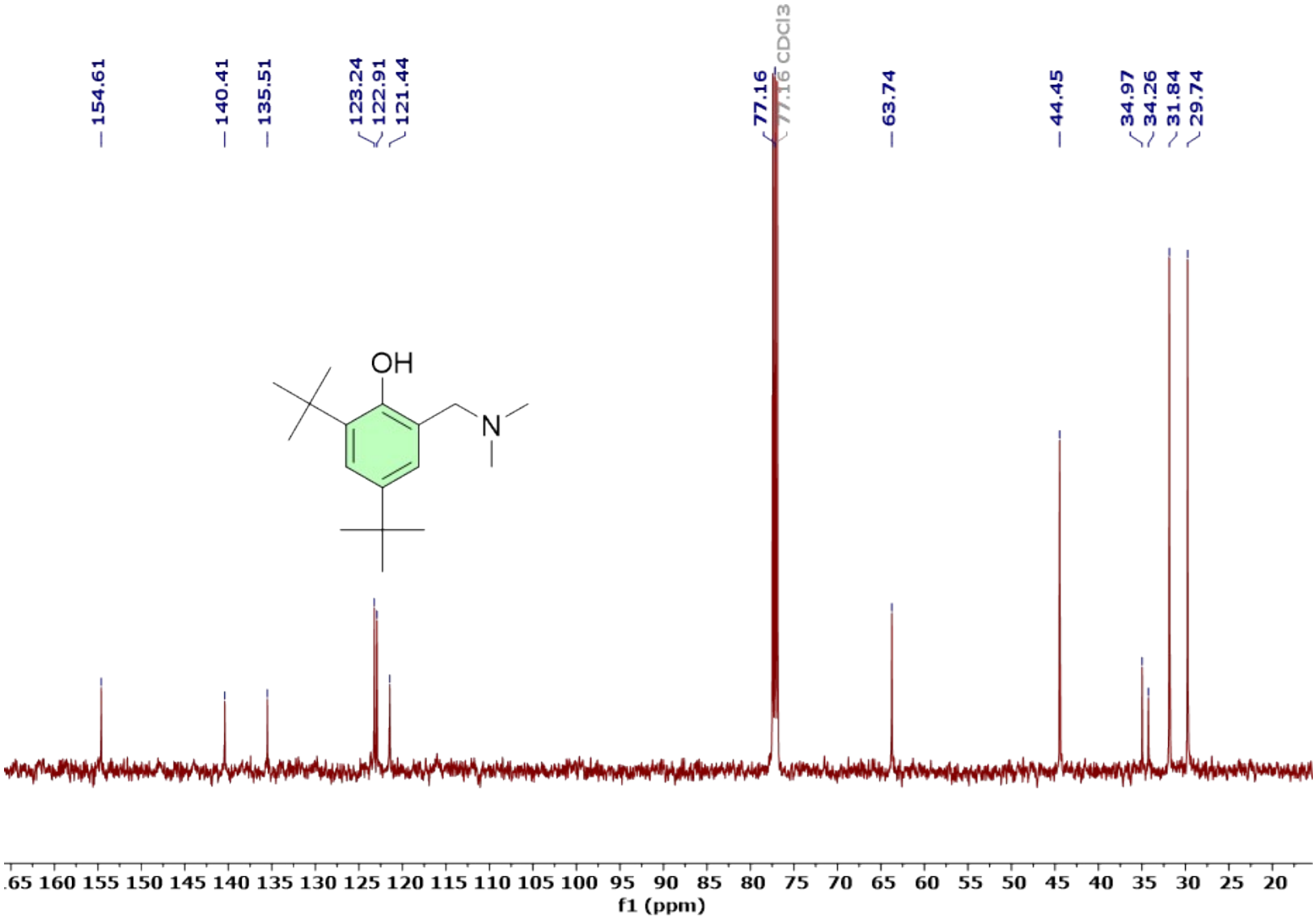


Fig. S14 ^{13}C NMR Spectrum of DMAMP (DMSO, 126 MHz, 298K)

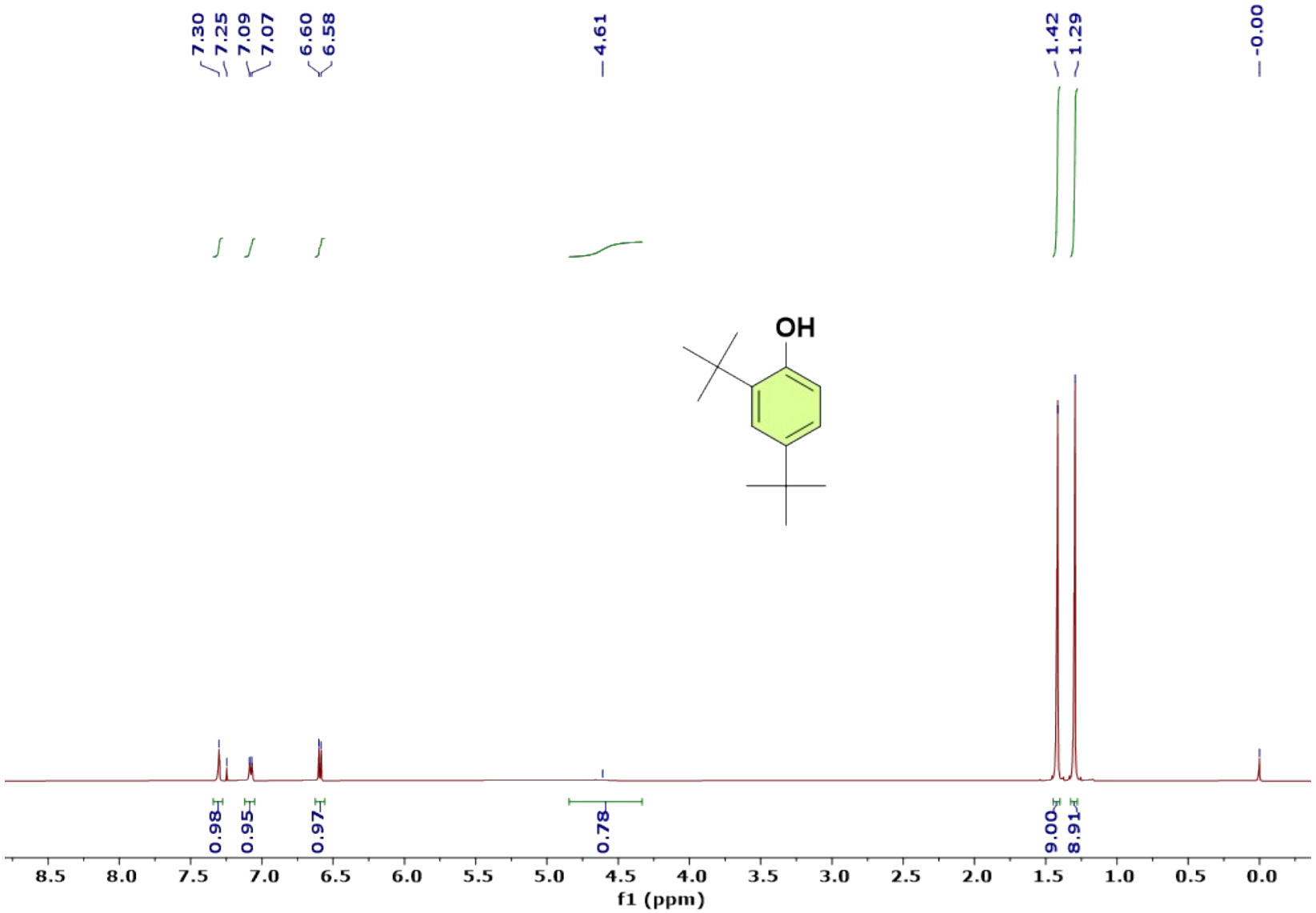


Fig. S15 ^{1}H NMR Spectrum of DTBP (DMSO, 500 MHz, 298K)

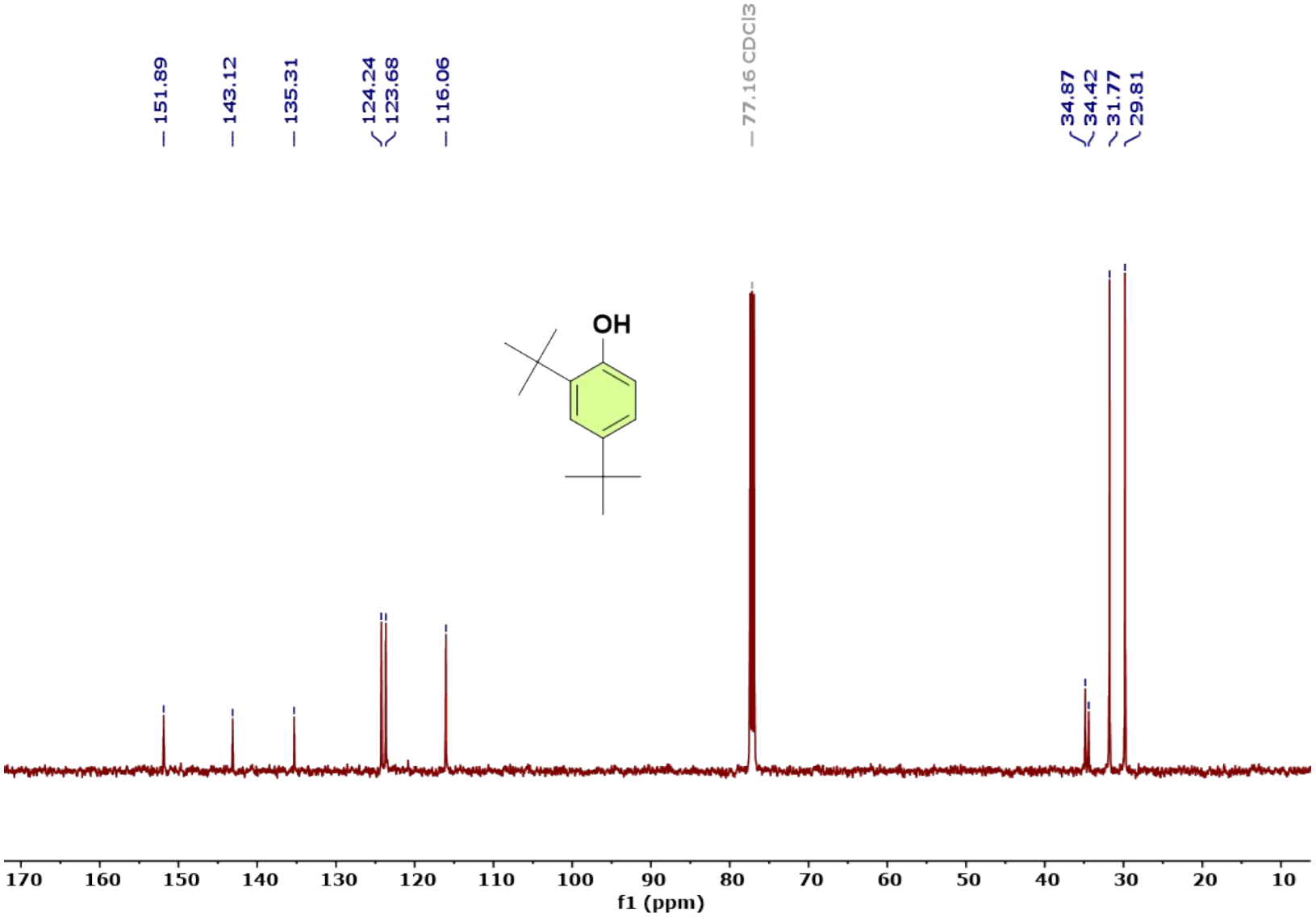


Fig. S16 ^{13}C NMR Spectrum of DTBP (DMSO, 126 MHz, 298K)

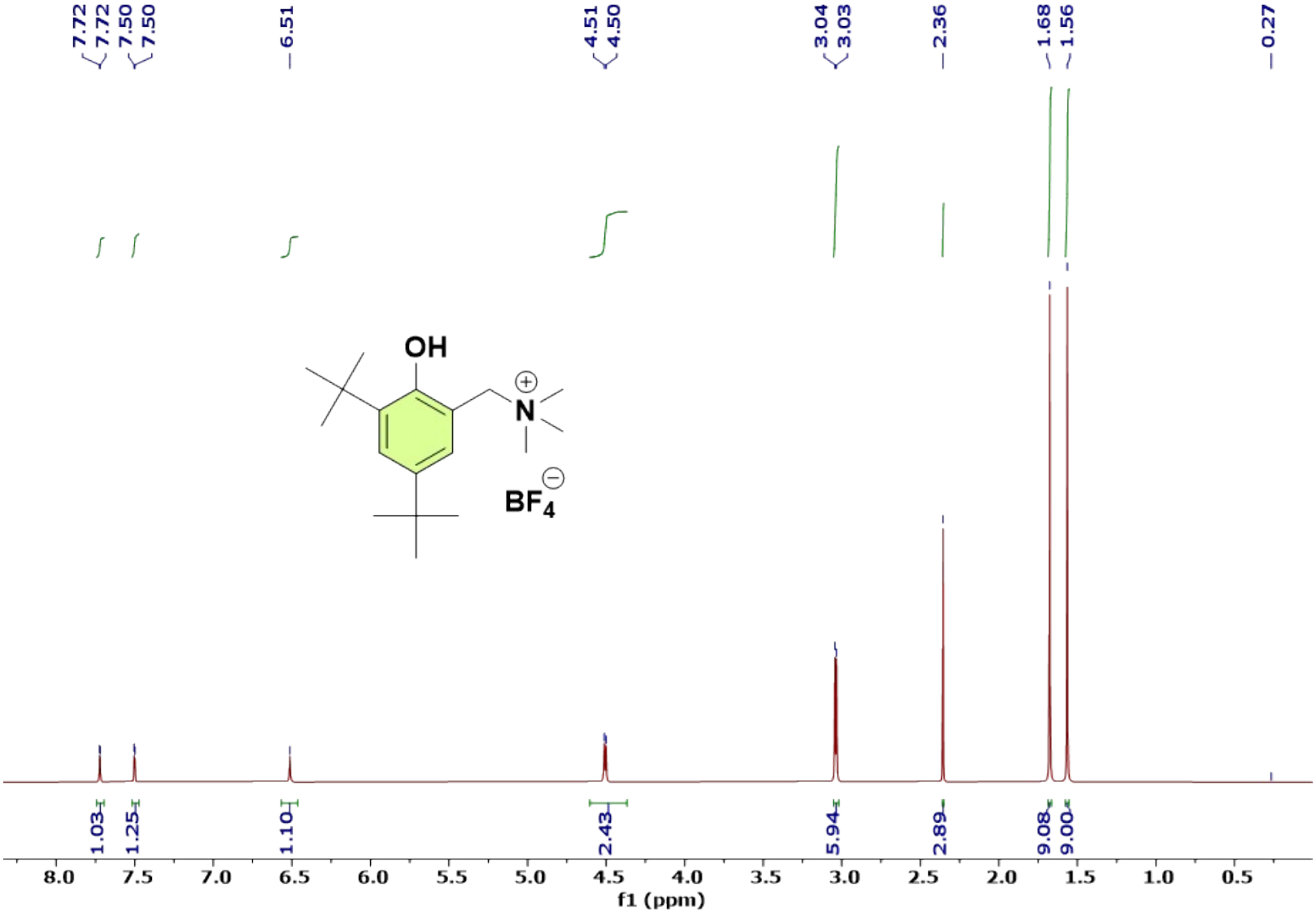


Fig. S17 ^{1}H NMR Spectrum of ETP-6(DMSO, 500 MHz, 298K)

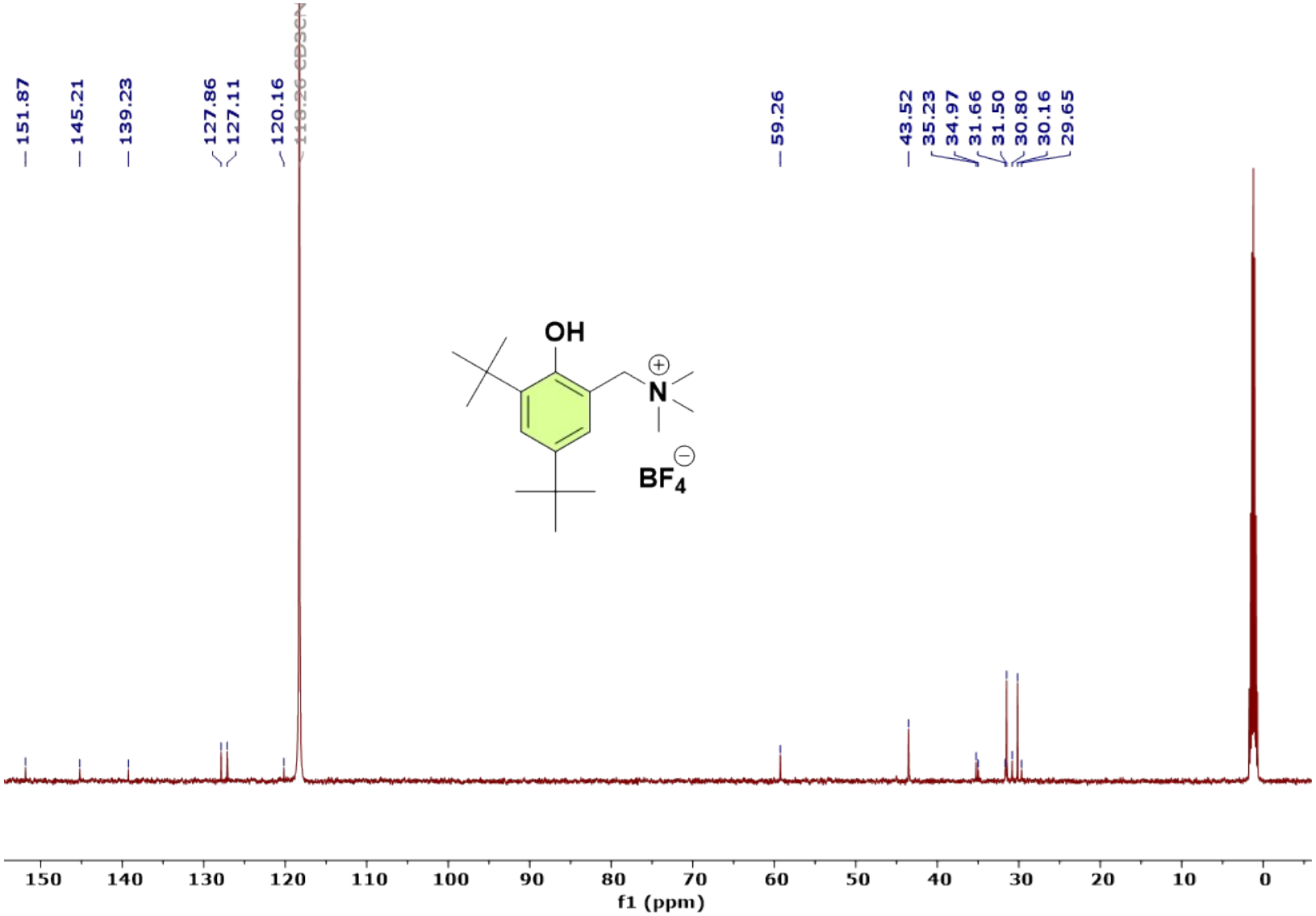


Fig. S18 ^{13}C NMR Spectrum of ETP-6 (DMSO, 126 MHz, 298K)

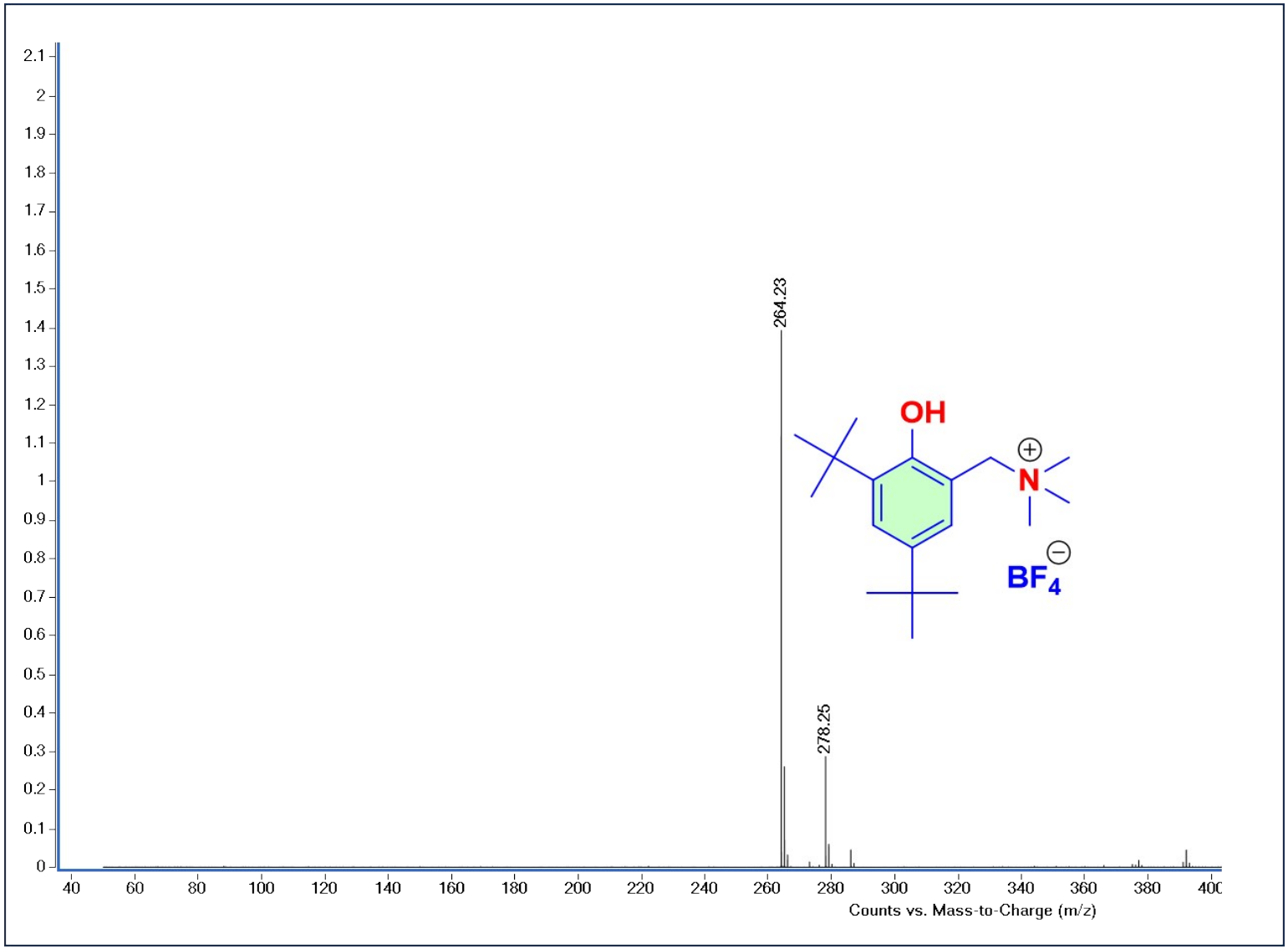


Fig. S19 HRMS Spectrum of ETP-6

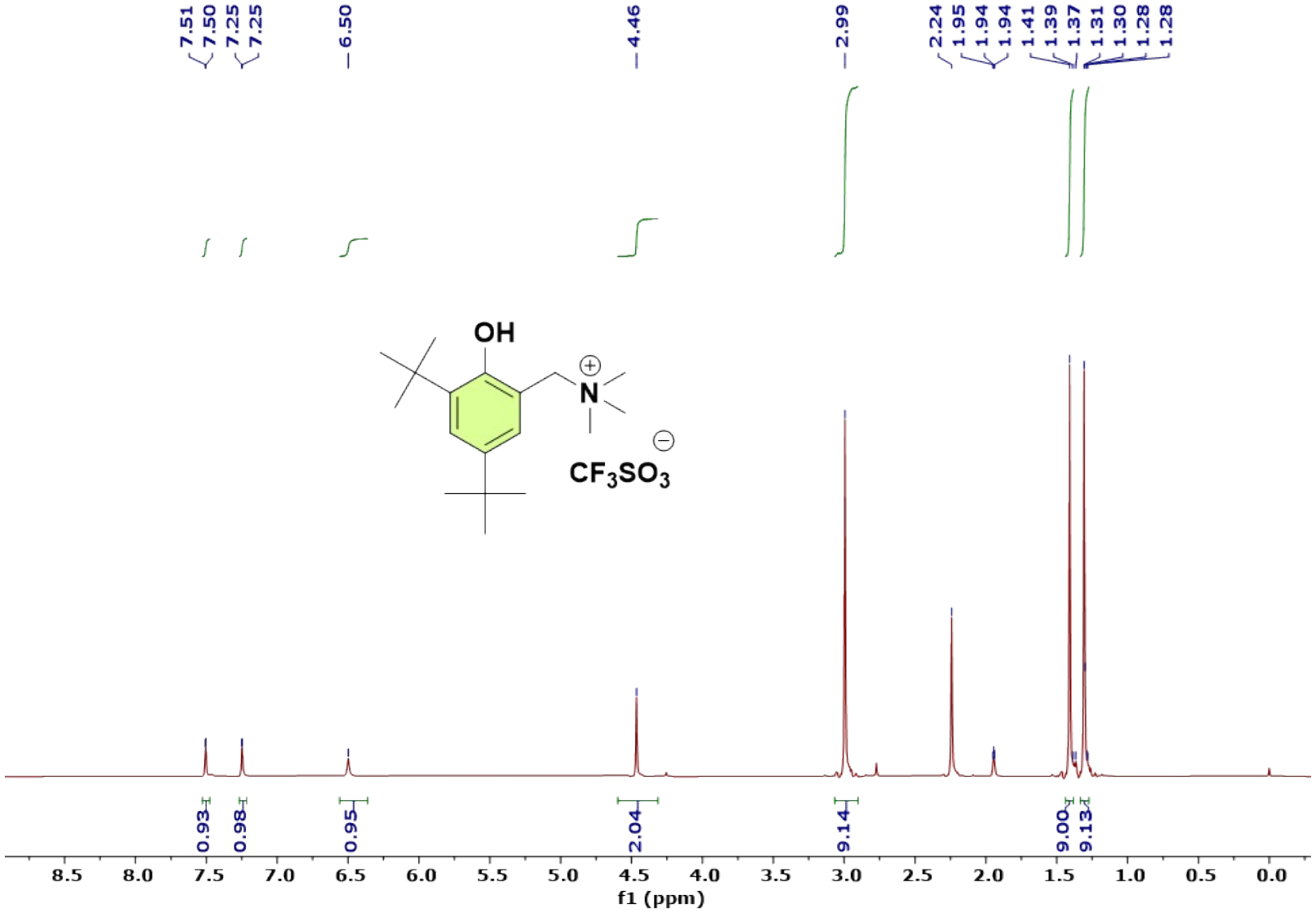


Fig. S20 ^{1}H NMR Spectrum of ETP-7 (DMSO, 500 MHz, 298K)

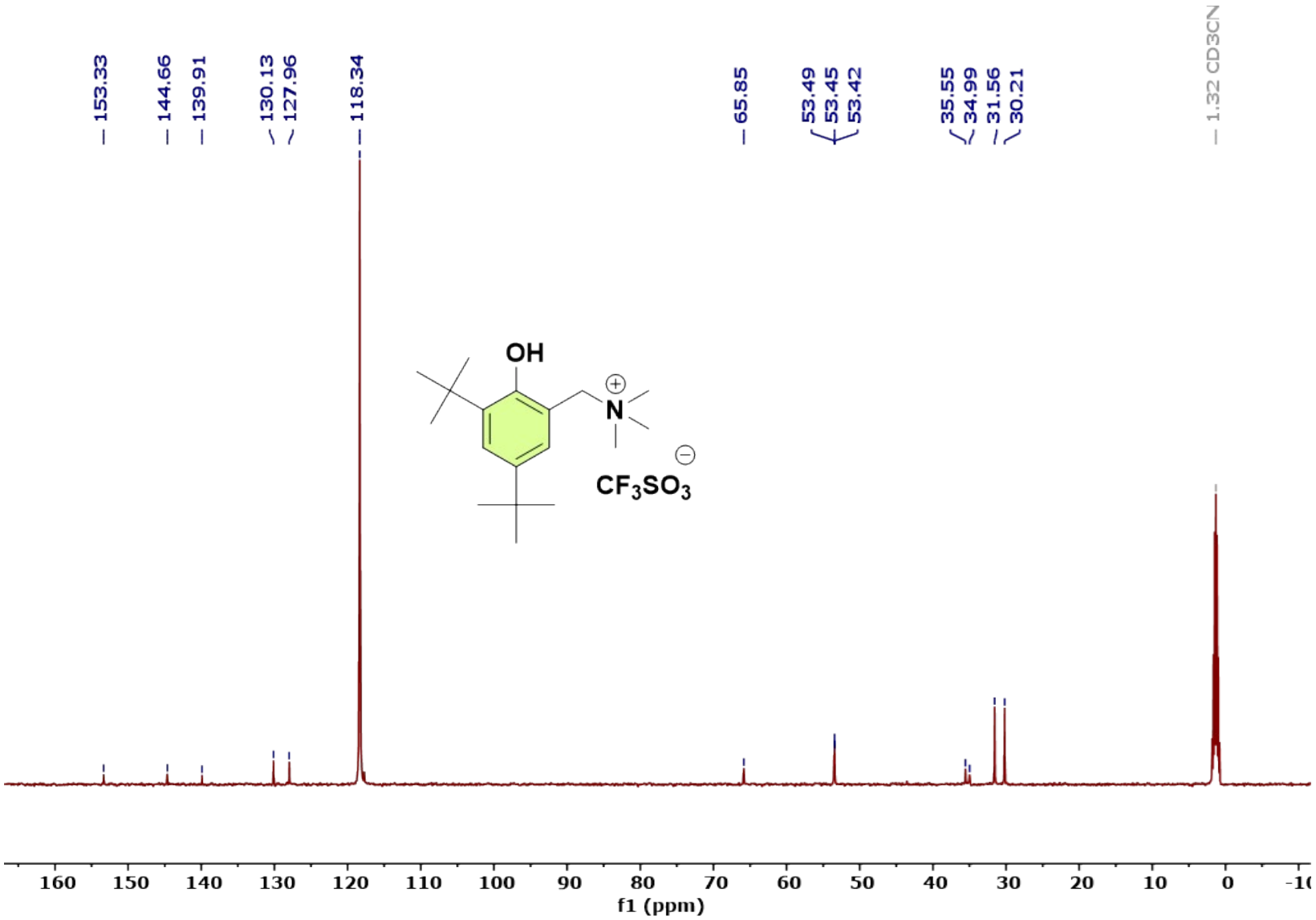


Fig. S21 ^{13}C NMR Spectrum of ETP-7 (DMSO, 126 MHz, 298K)

12. ^{1}H and ^{13}C NMR of julolidine Product

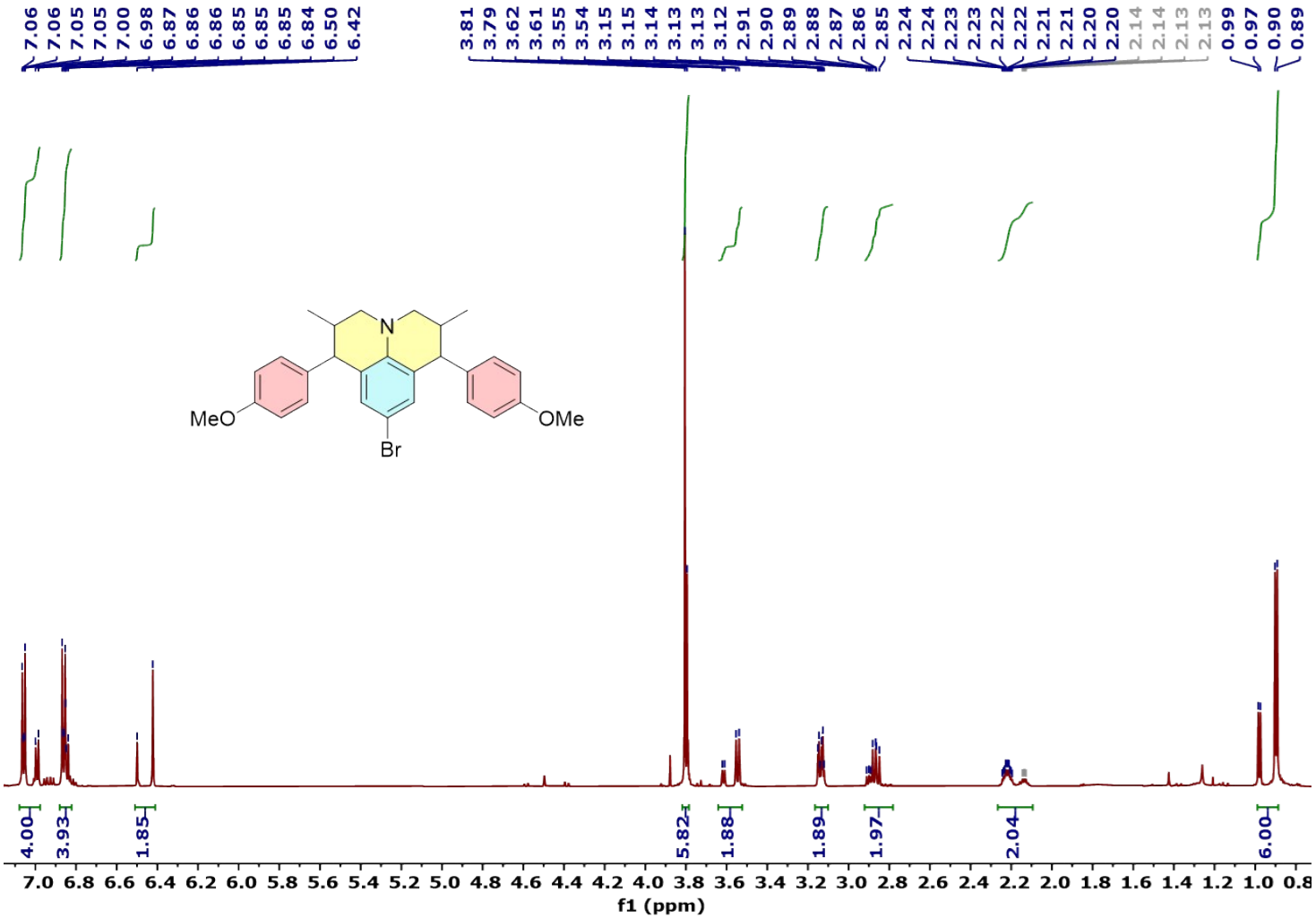


Fig. S22 ^{1}H NMR Spectrum of 9-bromo-1,7-bis(4-methoxyphenyl)-2,6-dimethyl-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline ($CDCl_3$, 600 MHz, 298K)

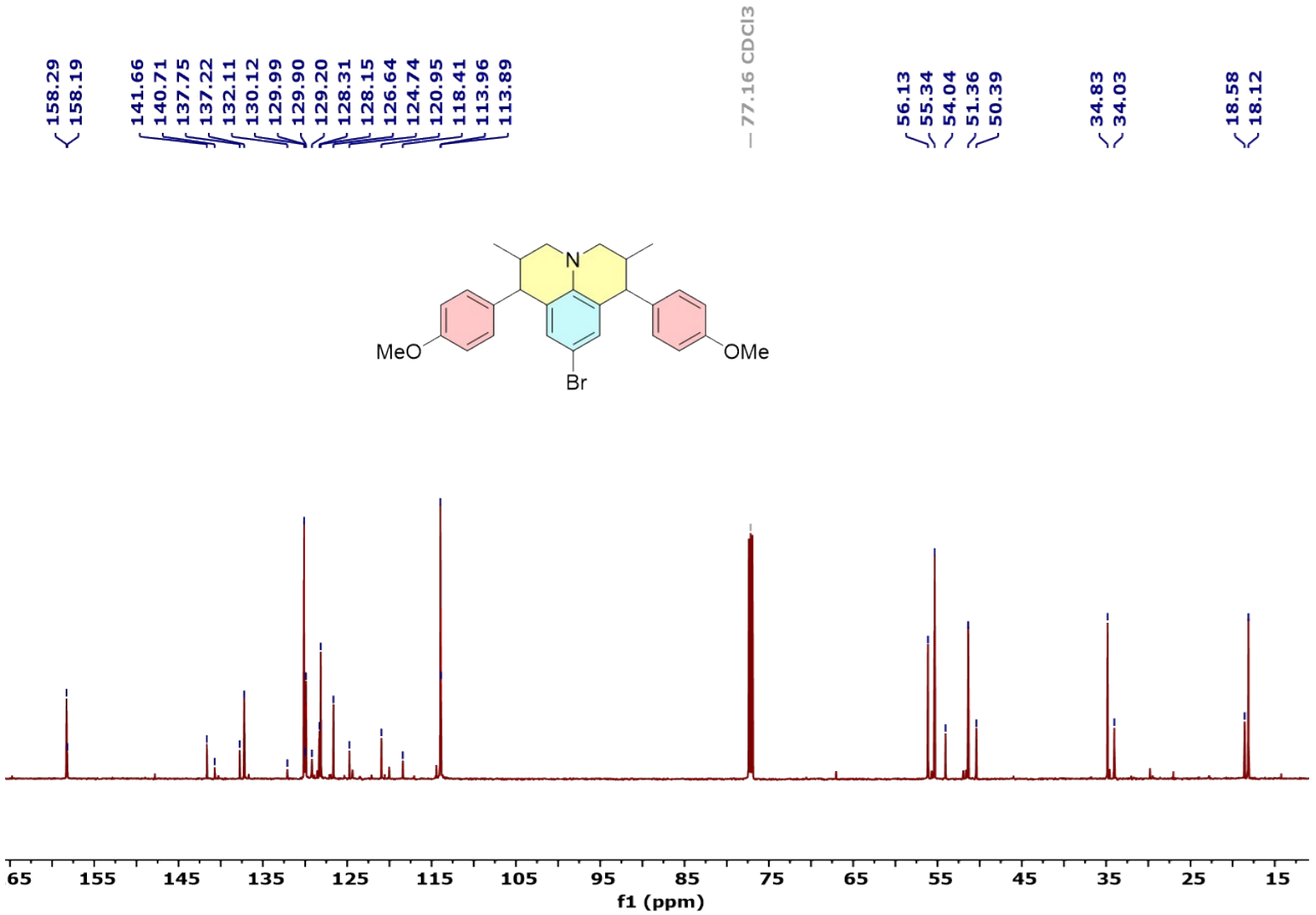


Fig. S23 ^{13}C NMR Spectrum of 9-bromo-1,7-bis(4-methoxyphenyl)-2,6-dimethyl-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline ($CDCl_3$, 151 MHz, 298K)

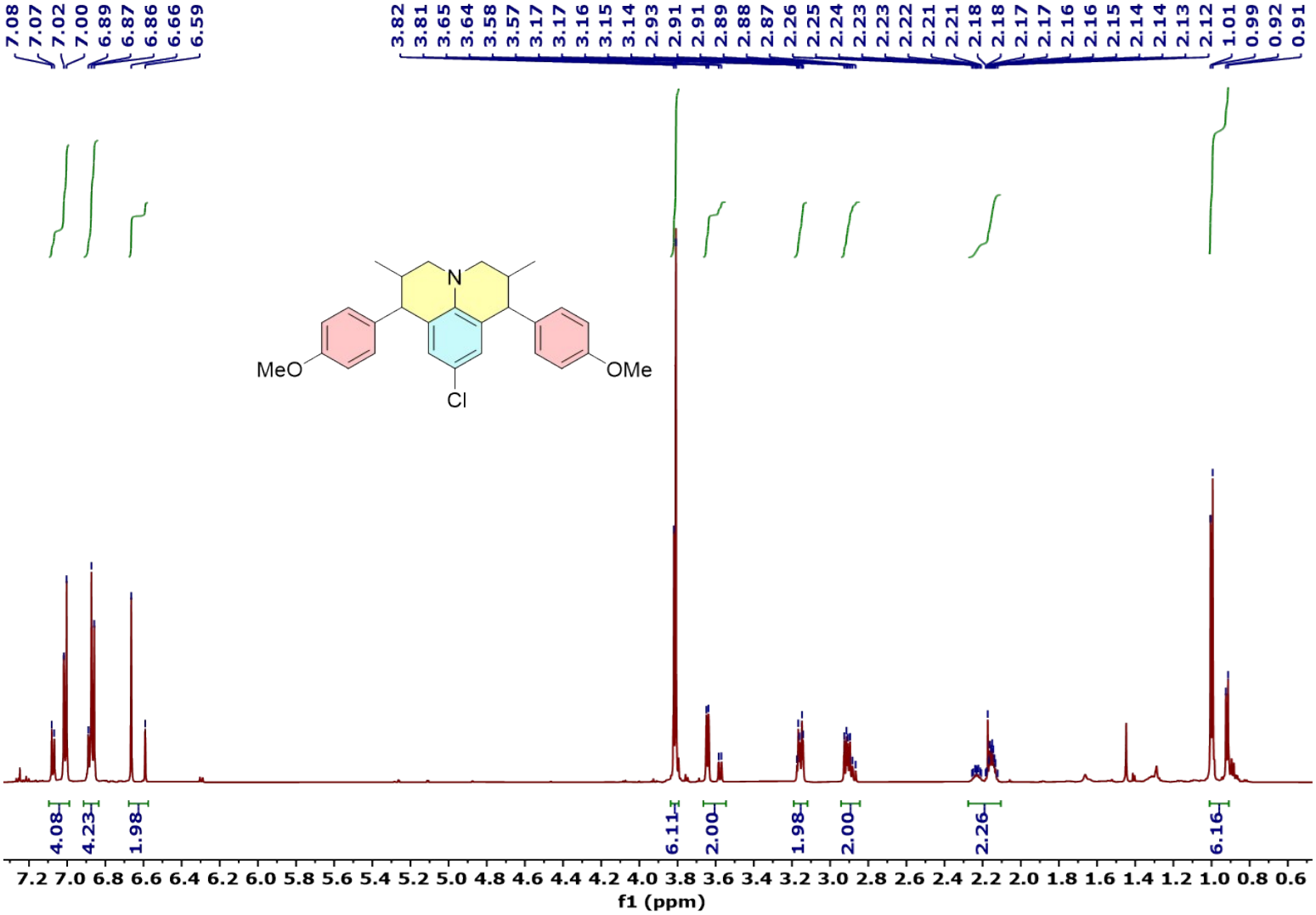


Fig. S24 ^{1}H NMR Spectrum of 9-chloro-1,7-bis(4-methoxyphenyl)-2,6-dimethyl-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline ($CDCl_3$, 600 MHz, 298K)

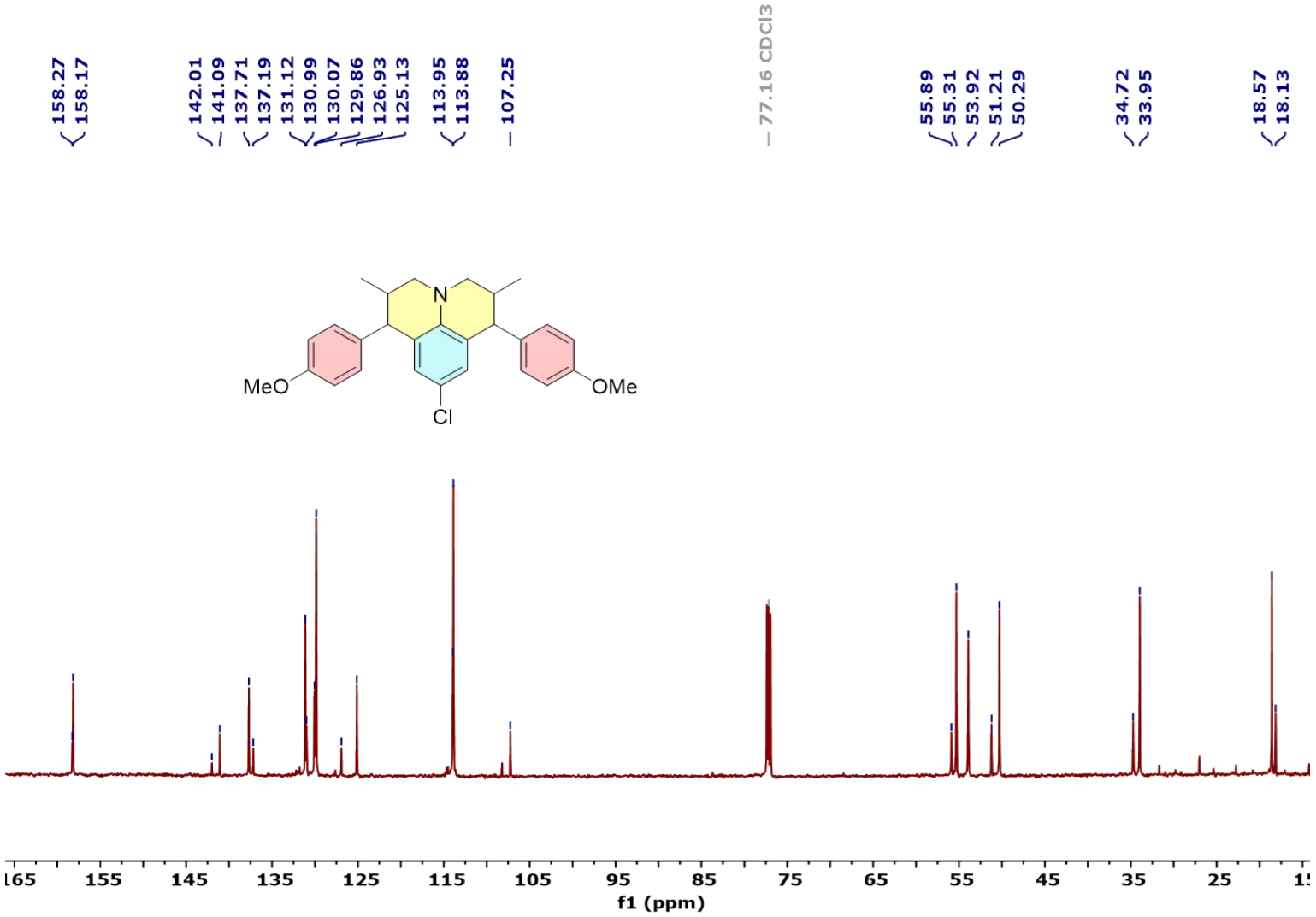


Fig. S25 ^{13}C NMR Spectrum of 9-chloro-1,7-bis(4-methoxyphenyl)-2,6-dimethyl-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline ($CDCl_3$, 151 MHz, 298K)

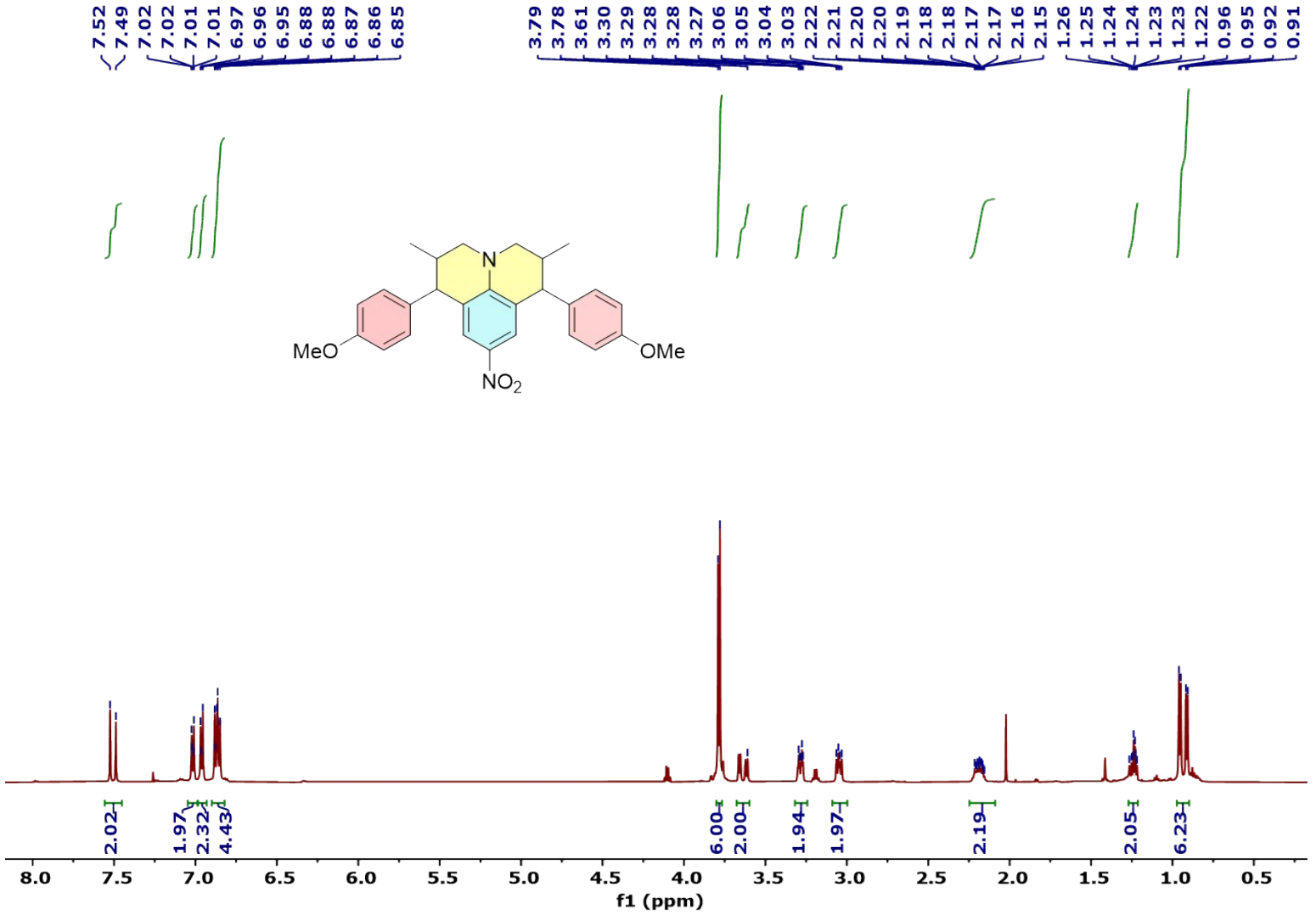


Fig. S26 ^{1}H NMR Spectrum of 1,7-bis(4-methoxyphenyl)-2,6-dimethyl-9-nitro-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline ($CDCl_3$, 600 MHz, 298K)

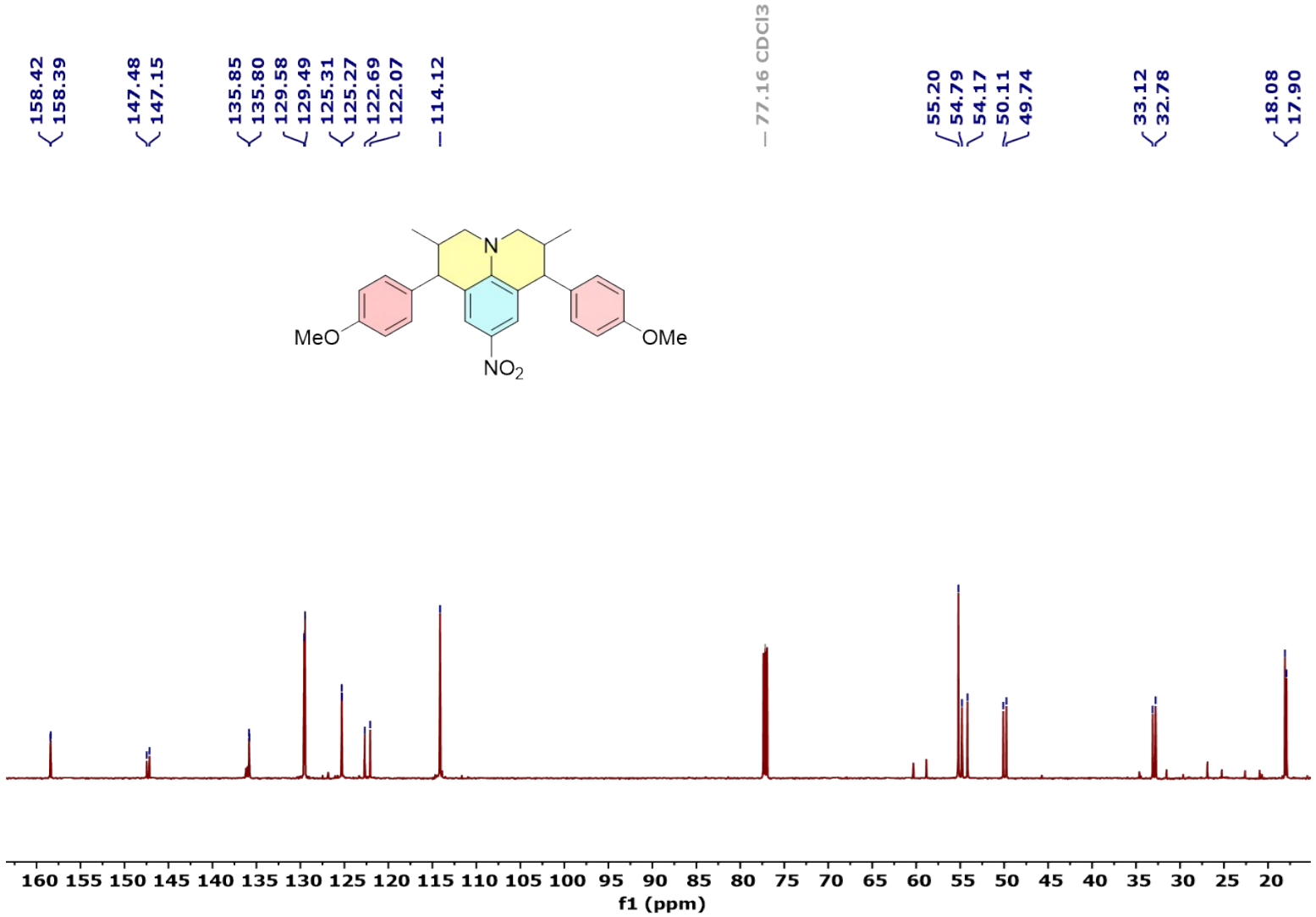


Fig. S27 ^{13}C NMR Spectrum of 1,7-bis(4-methoxyphenyl)-2,6-dimethyl-9-nitro-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline ($CDCl_3$, 151 MHz, 298K)

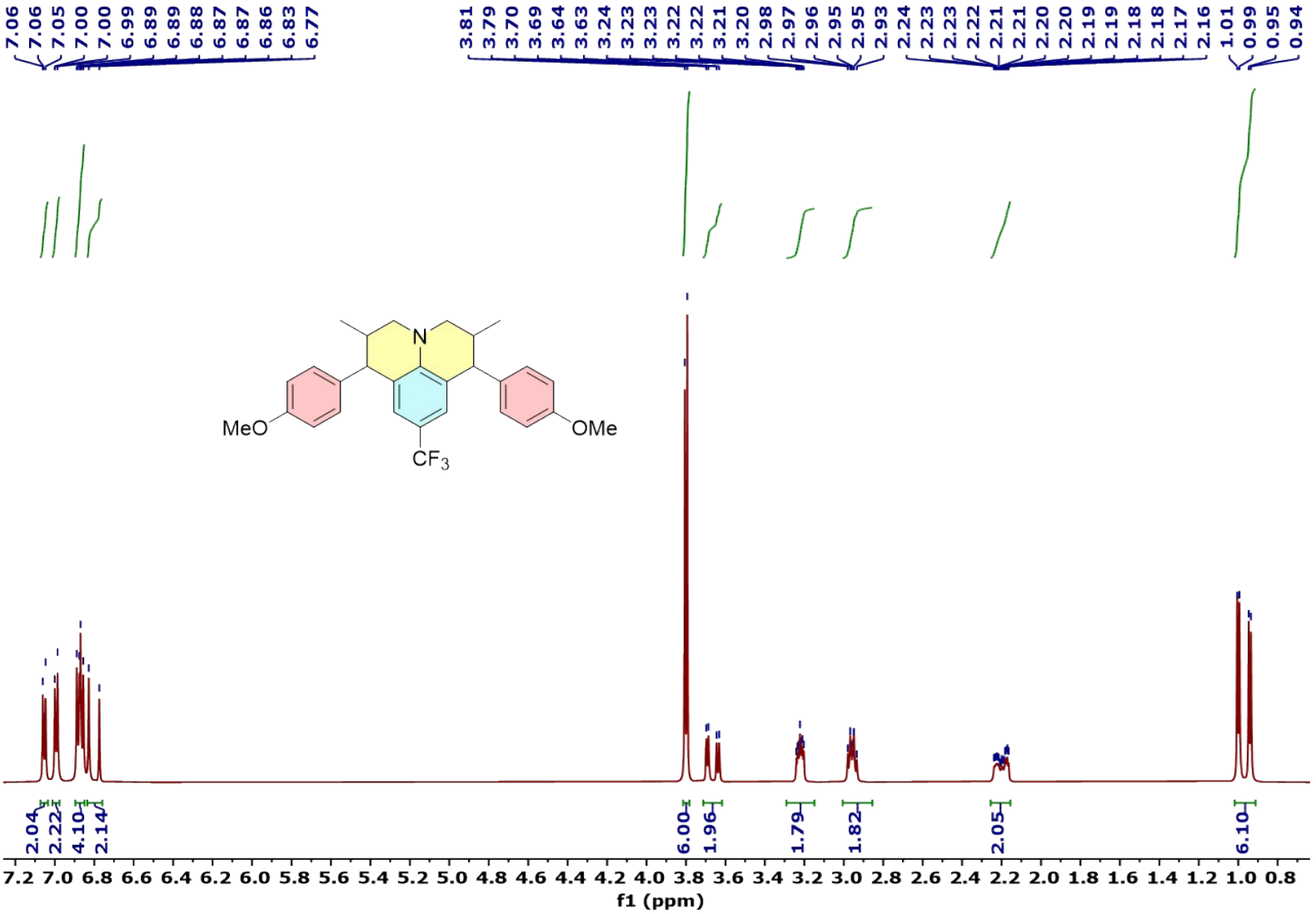


Fig. S28 ^{1}H NMR Spectrum of 1,7-bis(4-methoxyphenyl)-2,6-dimethyl-9-(trifluoromethyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline ($CDCl_3$, 600 MHz, 298K)

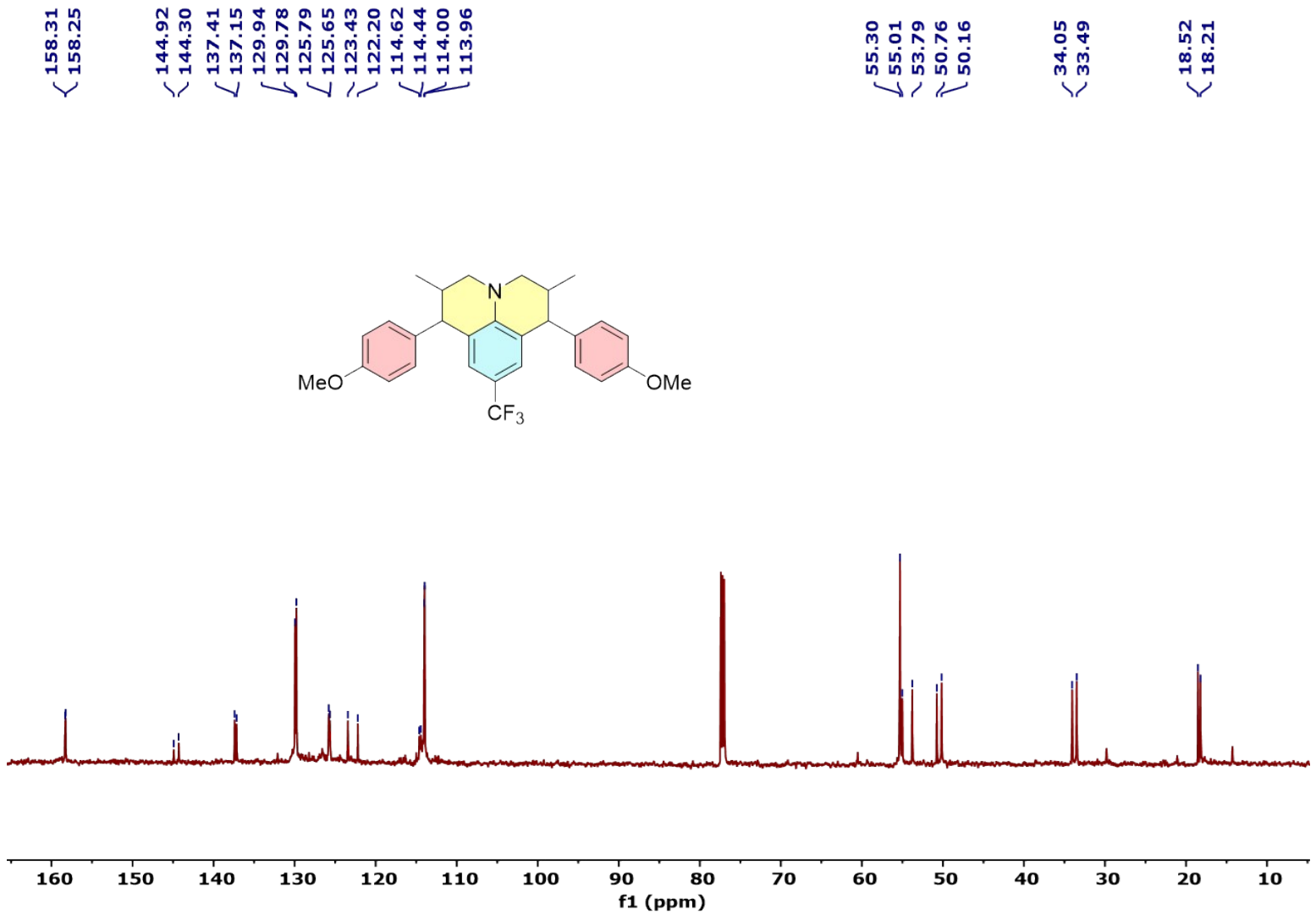


Fig. S29 ^{13}C NMR Spectrum of 1,7-bis(4-methoxyphenyl)-2,6-dimethyl-9-(trifluoromethyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline ($CDCl_3$, 150 MHz, 298K)

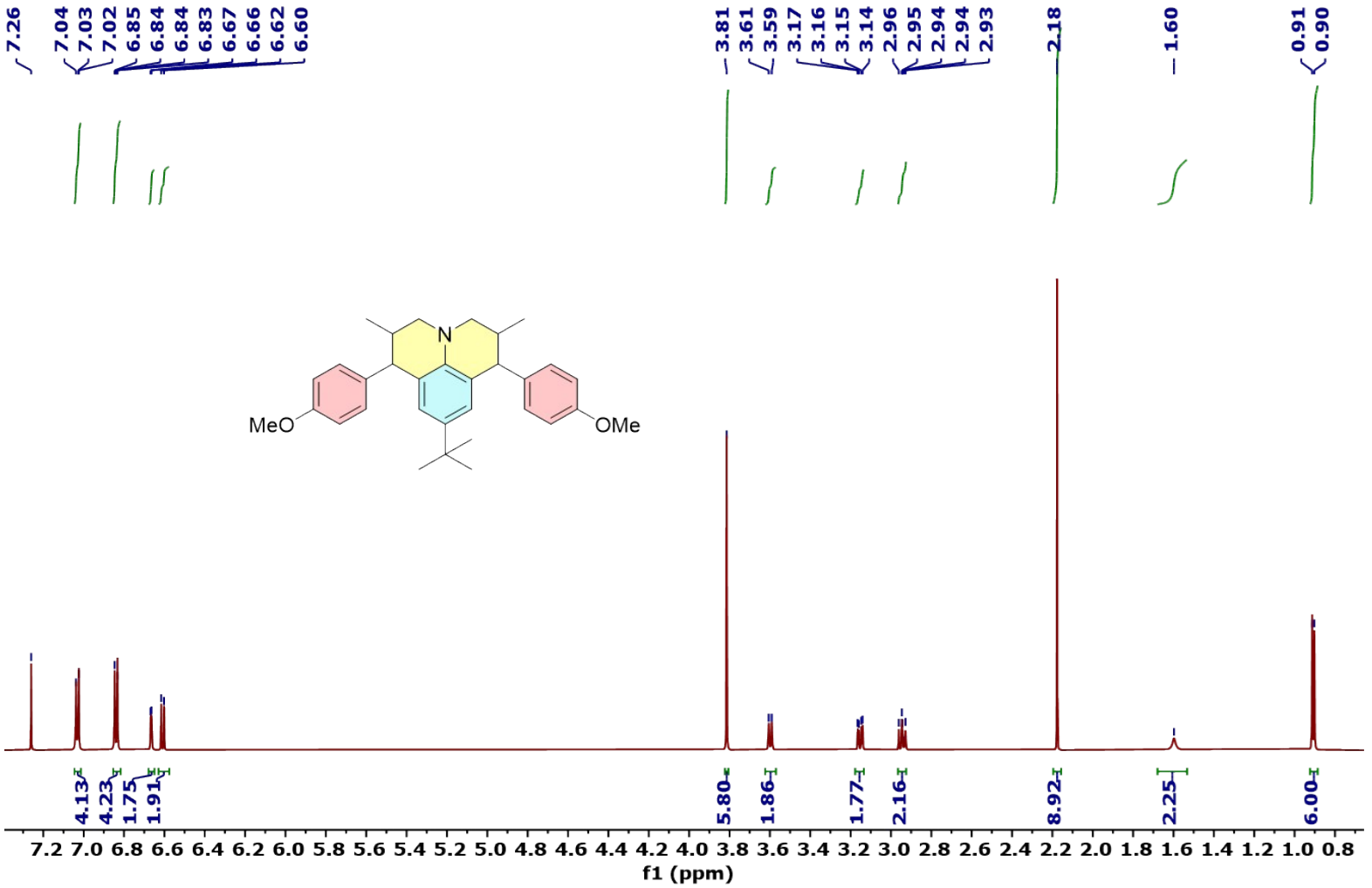


Fig. S30 ^{1}H NMR Spectrum of 9-(tert-butyl)-1,7-bis(4-methoxyphenyl)-2,6-dimethyl-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline ($CDCl_3$, 600 MHz, 298K)

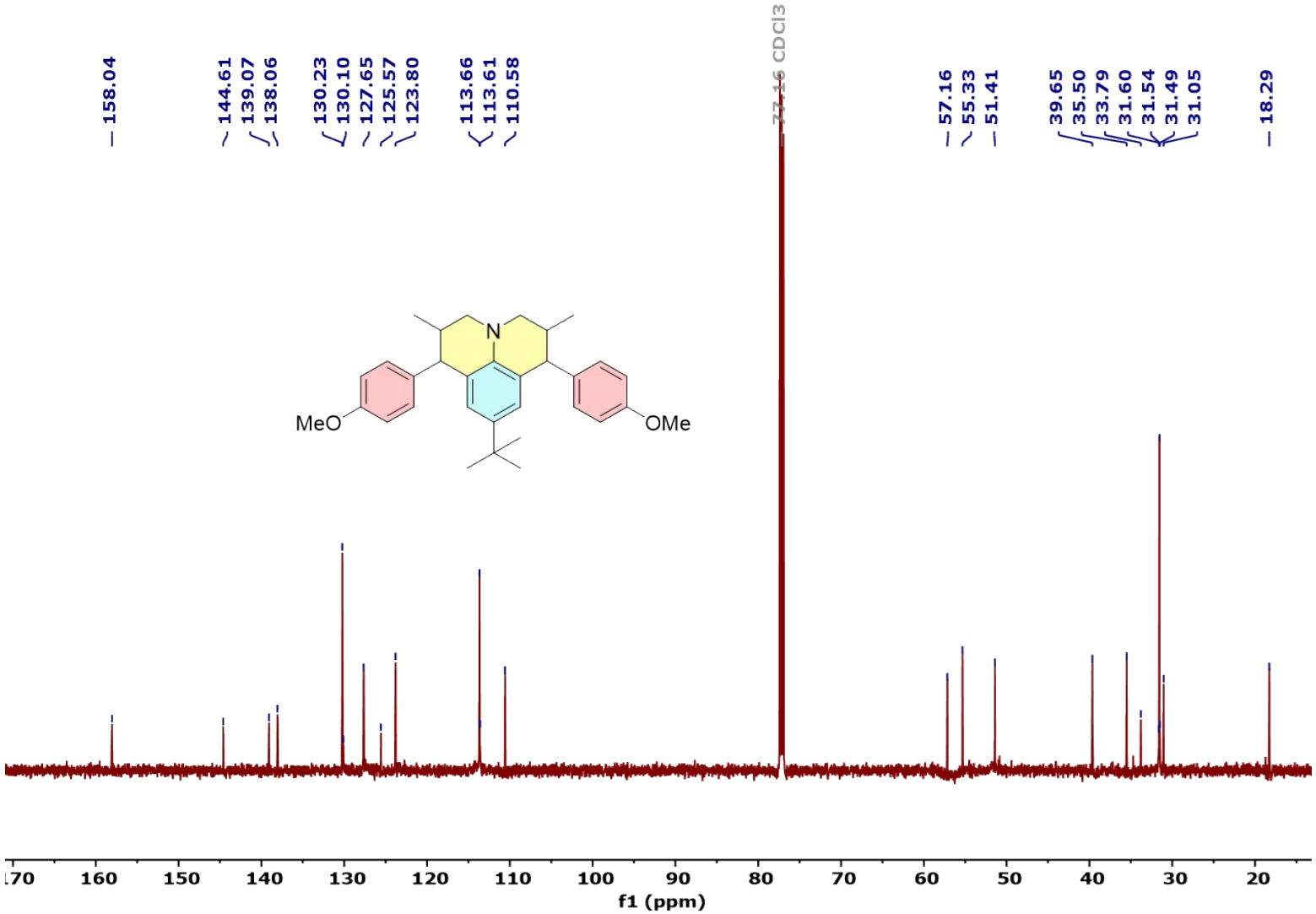


Fig. S31 ^{13}C NMR Spectrum of 9-(tert-butyl)-1,7-bis(4-methoxyphenyl)-2,6-dimethyl-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline ($CDCl_3$, 151 MHz, 298K)

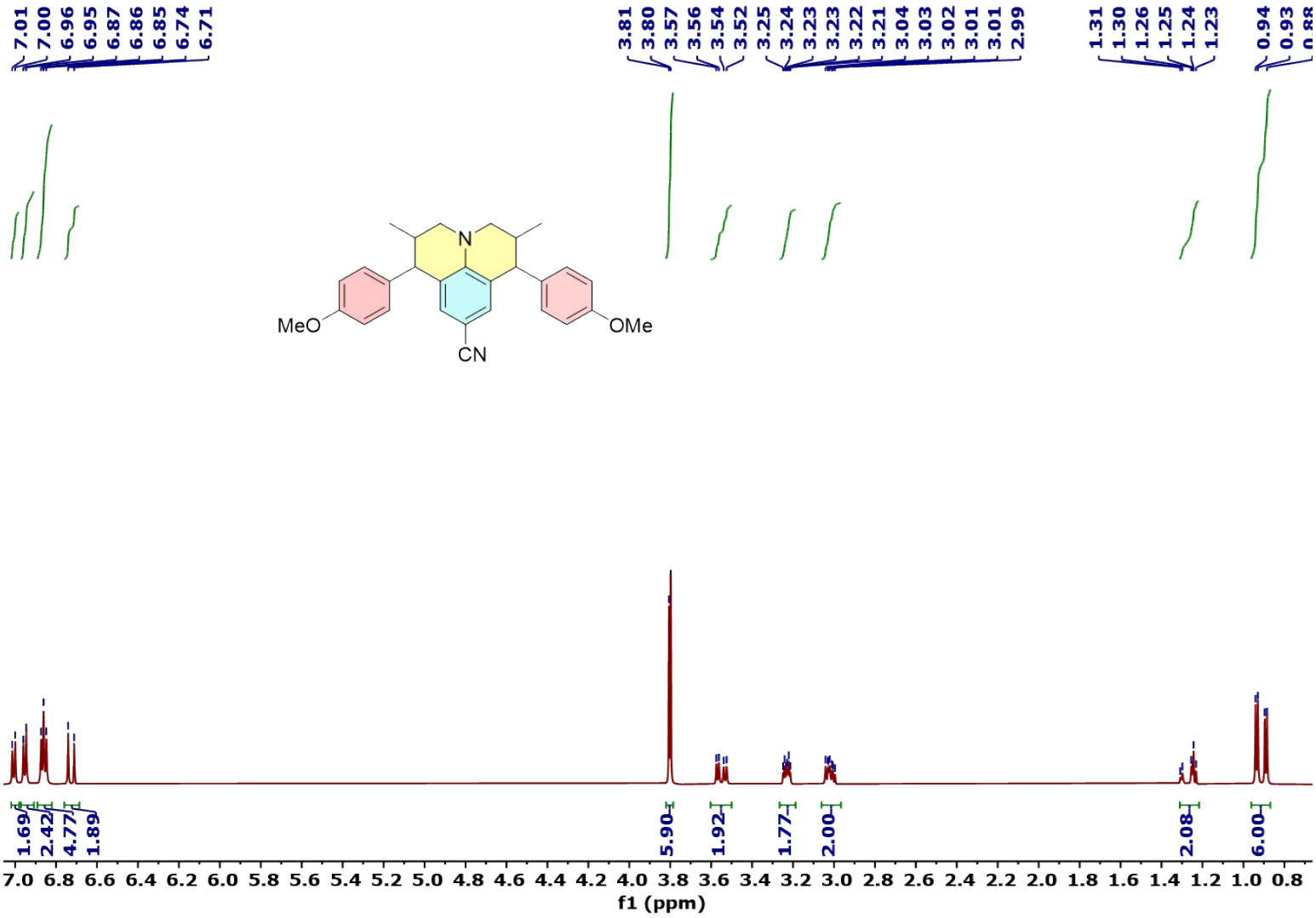


Fig. S32 ^{1}H NMR Spectrum of 1,7-bis(4-methoxyphenyl)-2,6-dimethyl-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline-9-carbonitrile ($CDCl_3$, 600 MHz, 298K)

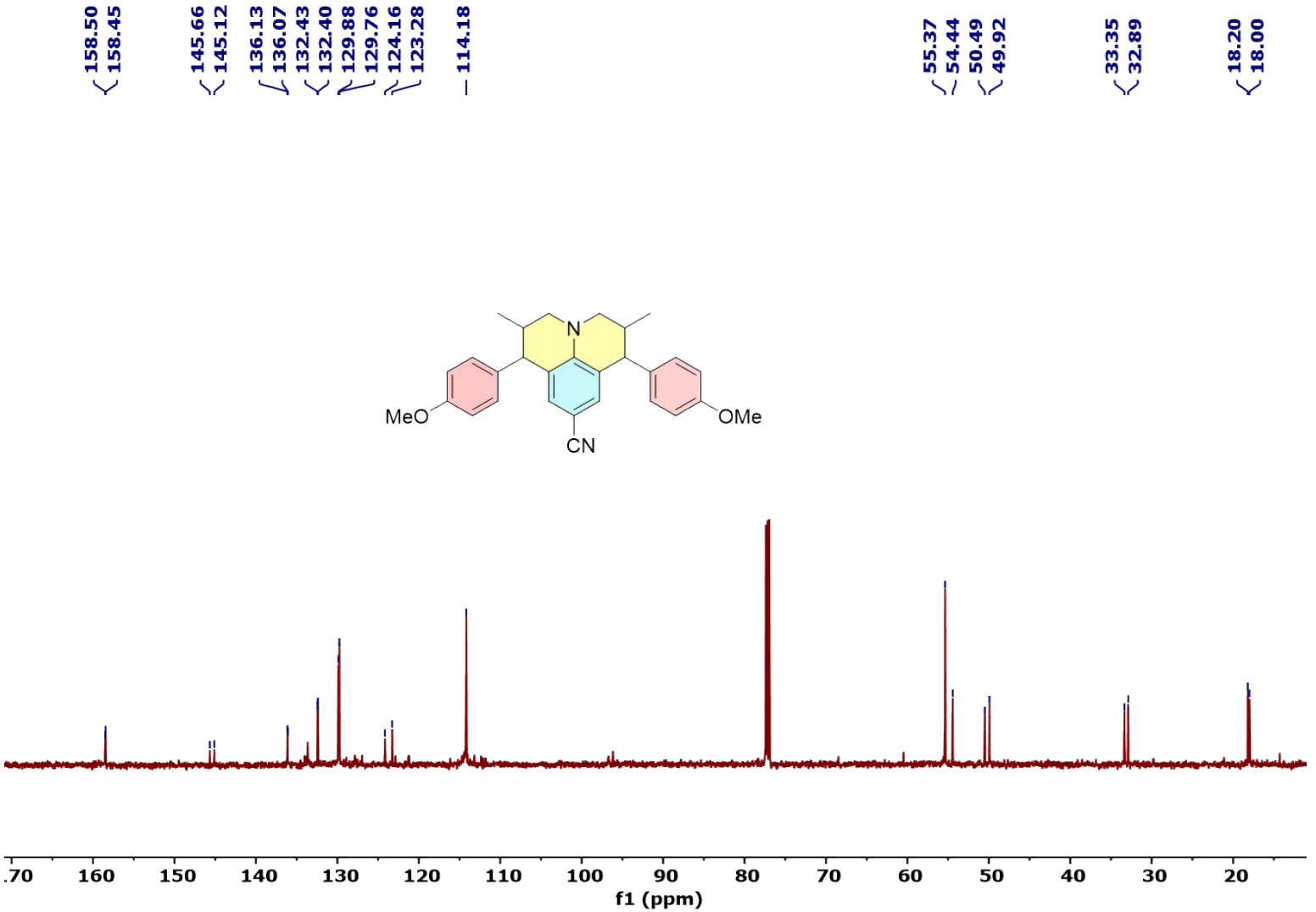


Fig. S33 ^{13}C NMR Spectrum of 1,7-bis(4-methoxyphenyl)-2,6-dimethyl-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline-9-carbonitrile ($CDCl_3$, 151 MHz, 298K)

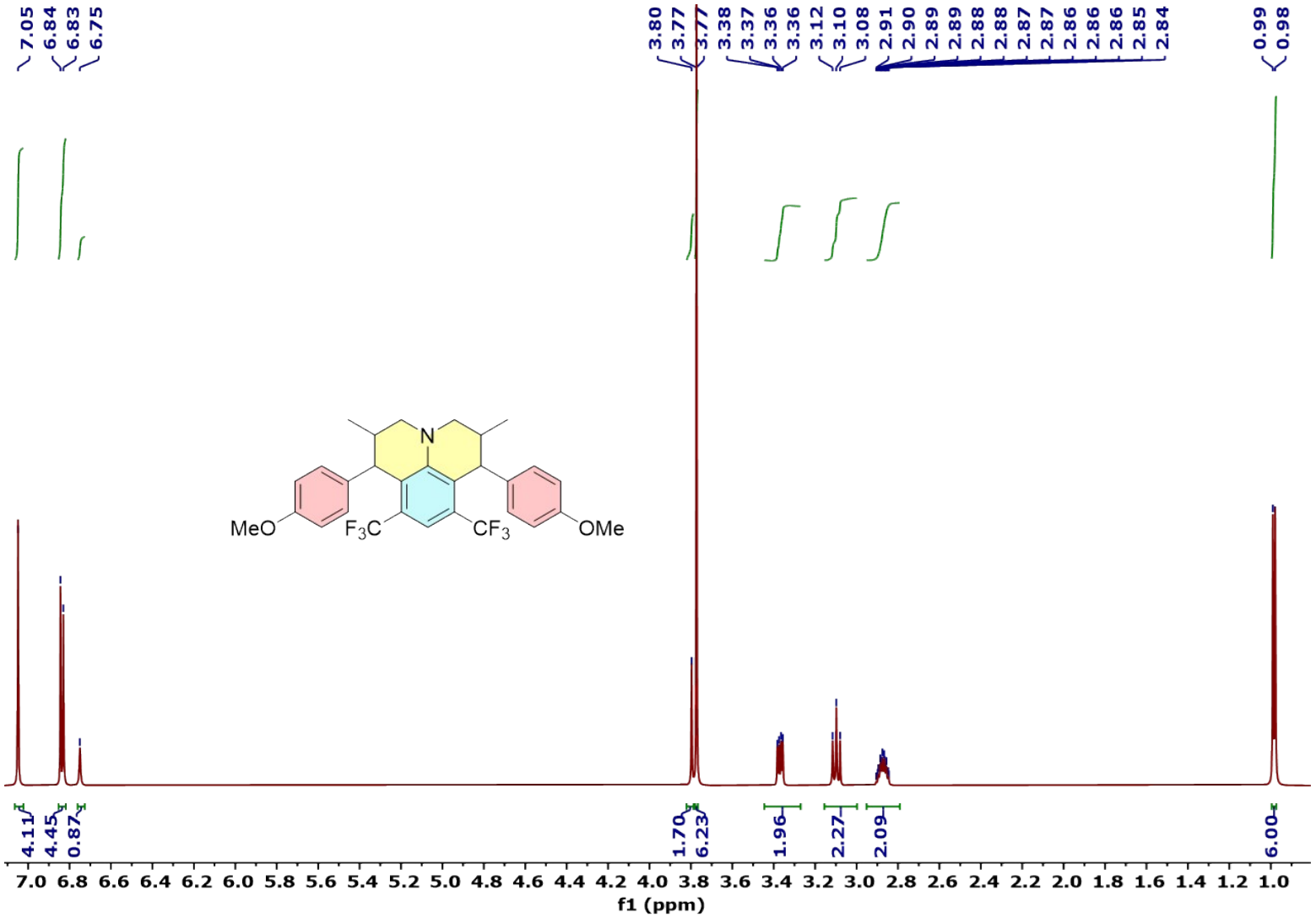


Fig. S34 ^{1}H NMR Spectrum of 1,7-bis(4-methoxyphenyl)-2,6-dimethyl-8,10-bis(trifluoromethyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline ($CDCl_3$, 600 MHz, 298K)

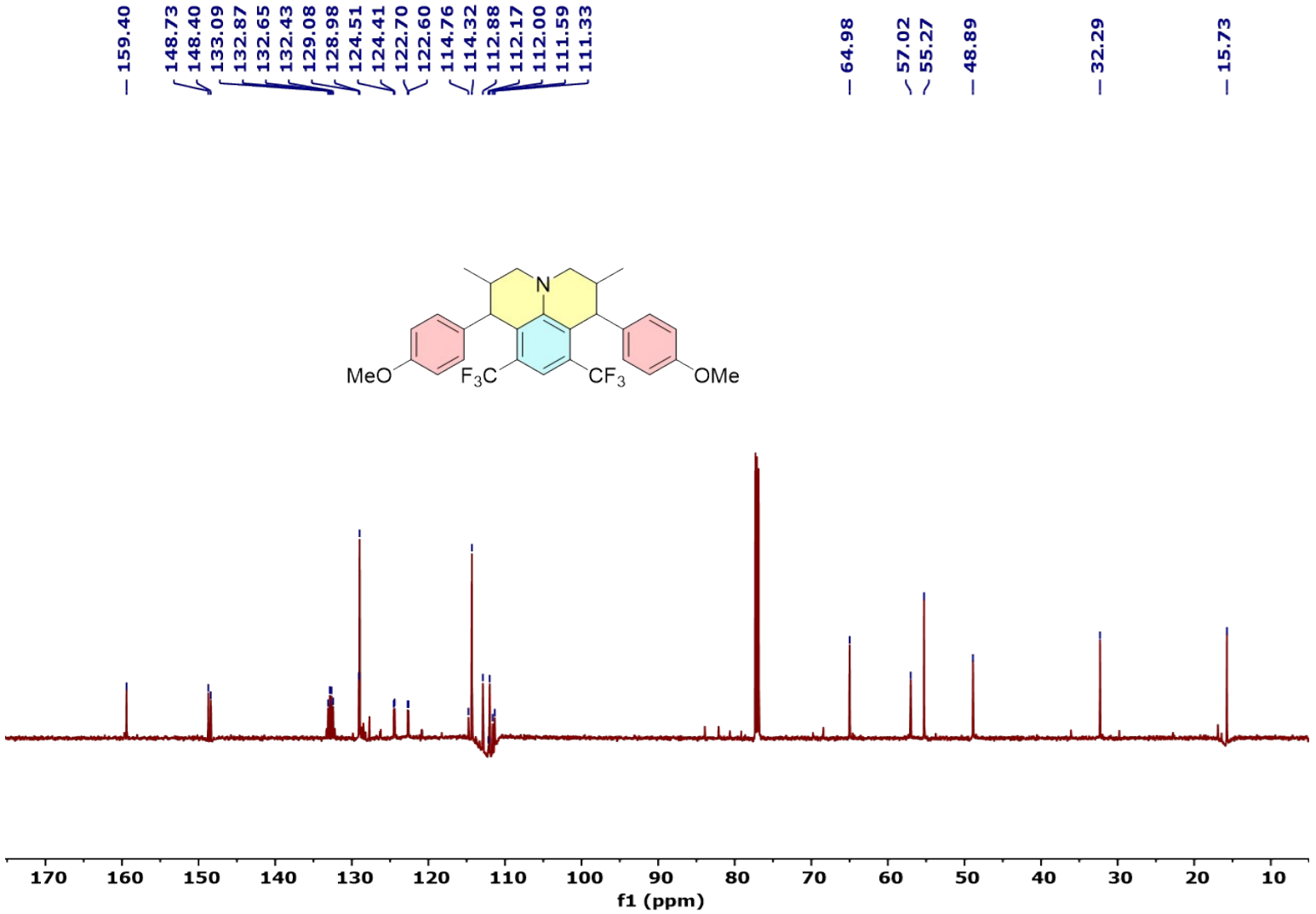


Fig. S35 ^{13}C NMR Spectrum of 1,7-bis(4-methoxyphenyl)-2,6-dimethyl-8,10-bis(trifluoromethyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline ($CDCl_3$, 151 MHz, 298K)

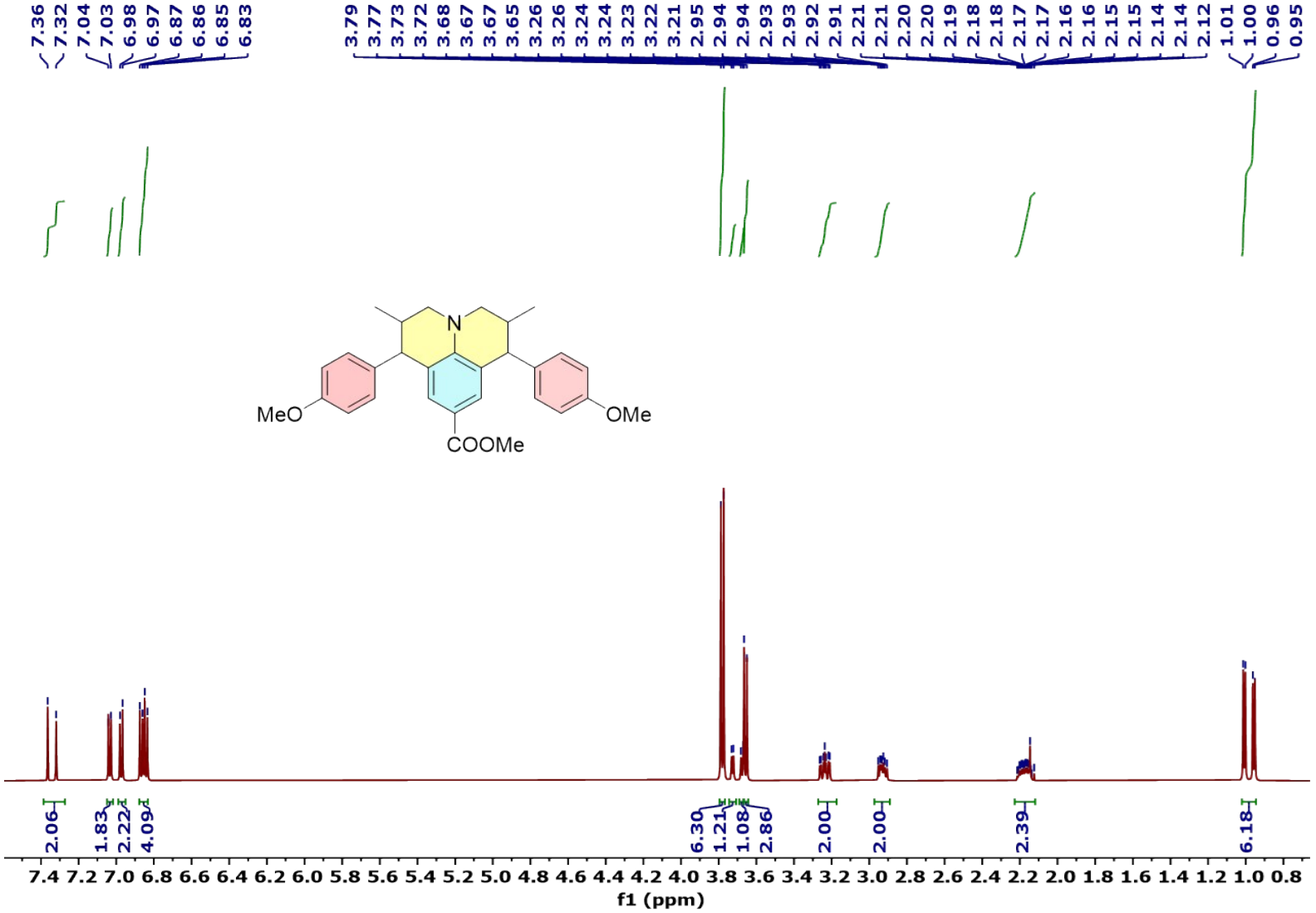


Fig. S36 ^{1}H NMR Spectrum of Methyl1,7-bis(4-methoxyphenyl)-2,6-dimethyl-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline-9-carboxylate ($CDCl_3$, 600 MHz, 298K)

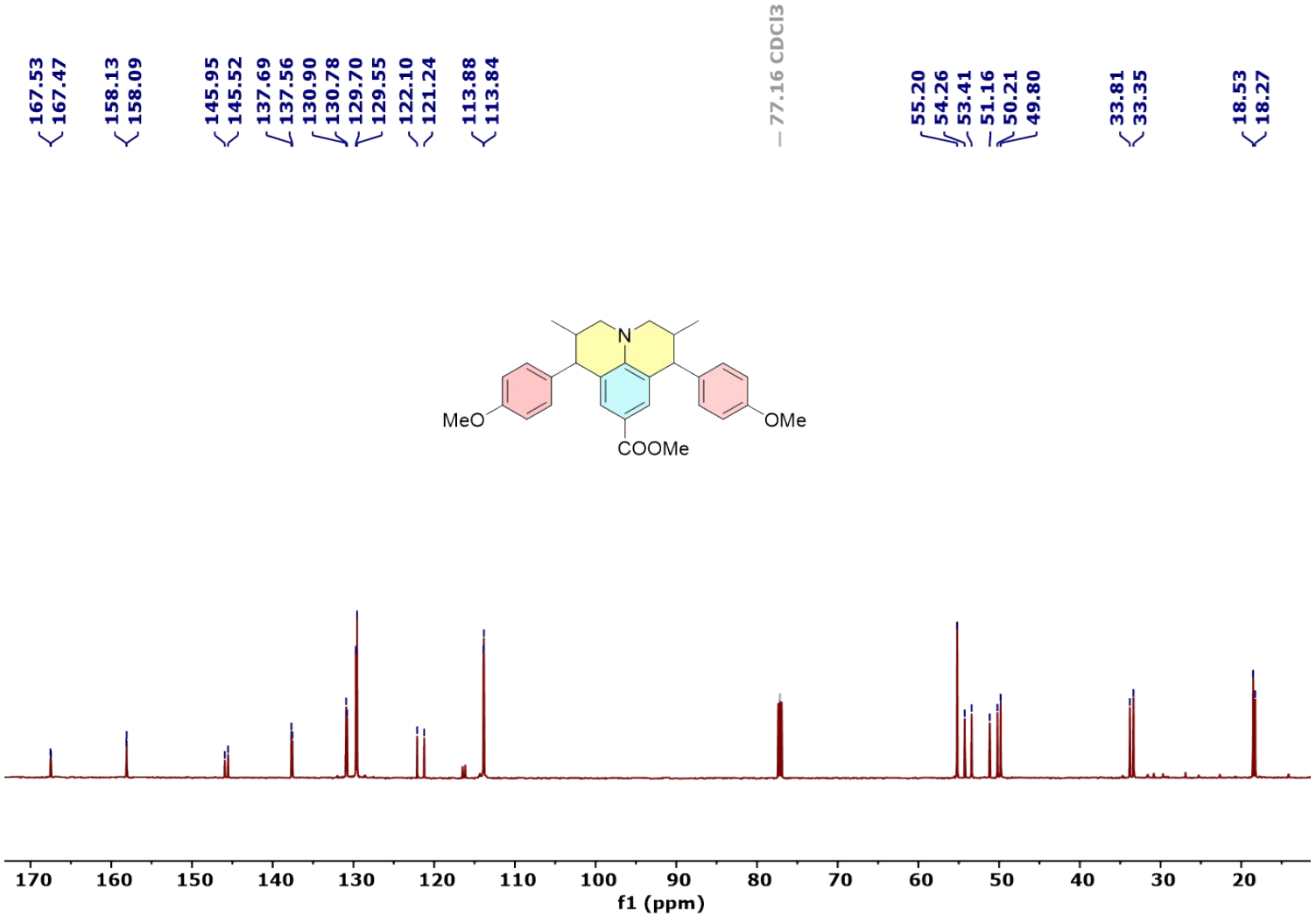


Fig. S37 ^{13}C NMR Spectrum of Methyl1,7-bis(4-methoxyphenyl)-2,6-dimethyl-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline-9-carboxylate ($CDCl_3$, 151 MHz, 298K)

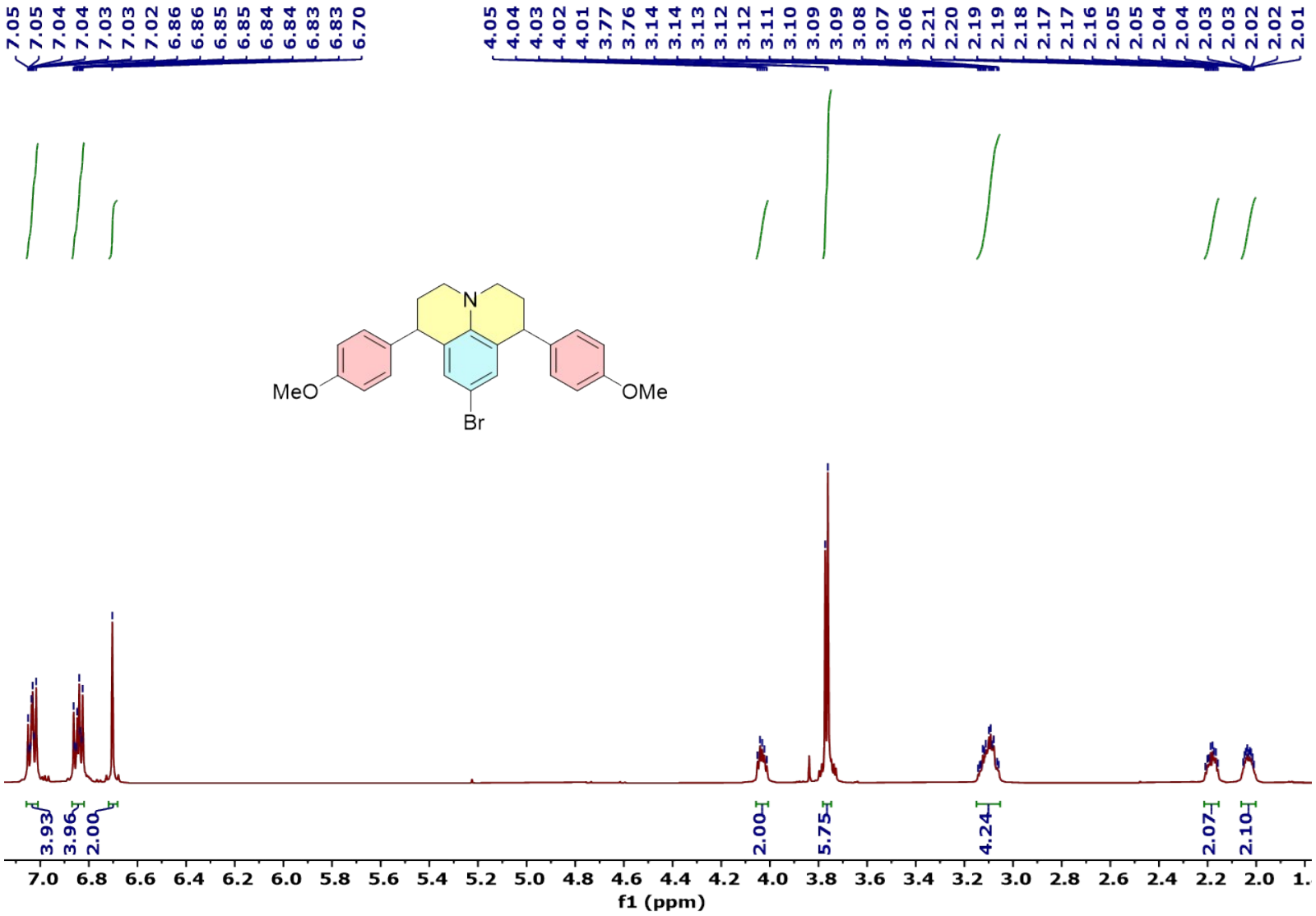


Fig. S38 ^{1}H NMR Spectrum of 9-bromo-1,7-bis(4-methoxyphenyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline ($CDCl_3$, 600 MHz, 298K)

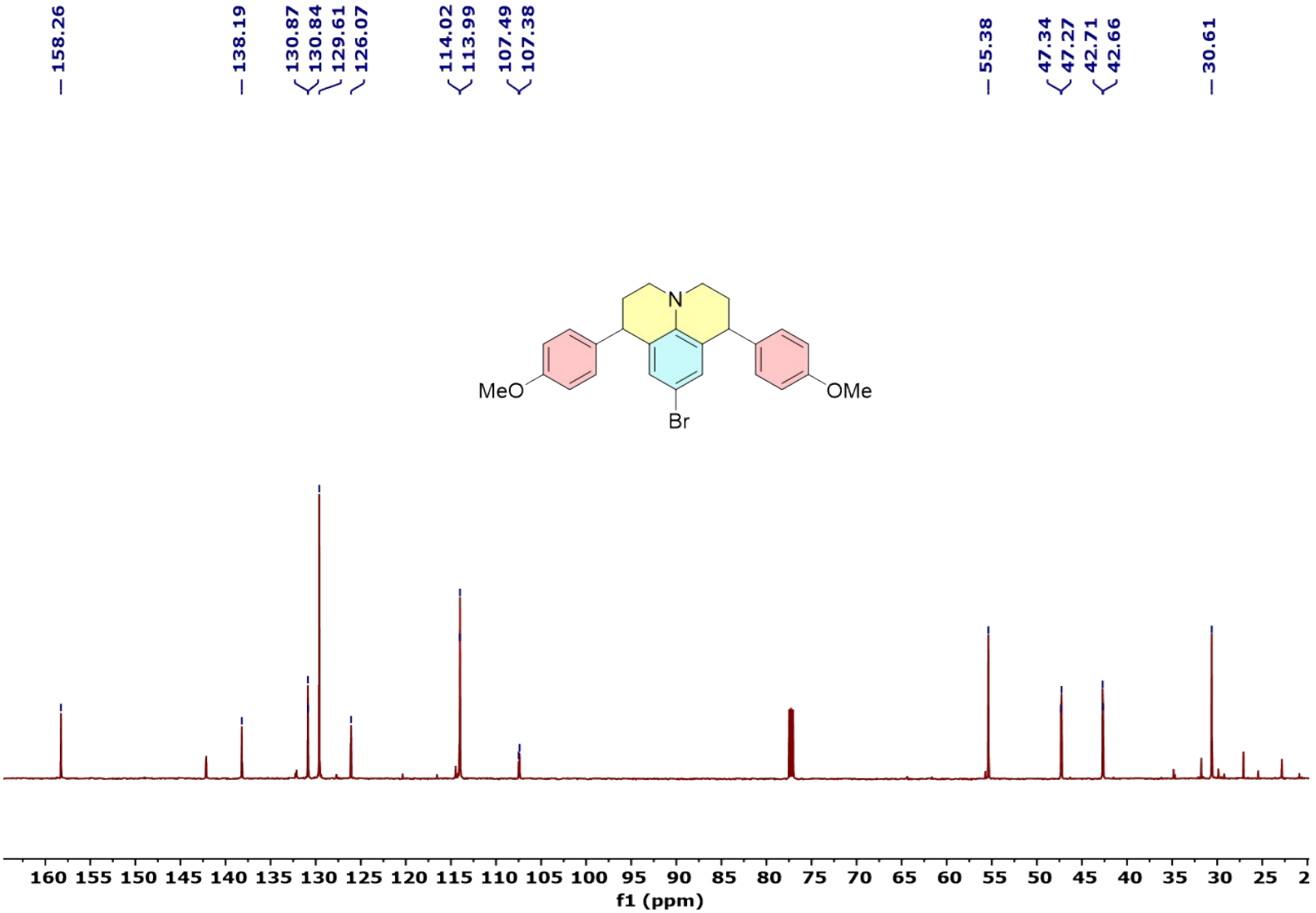


Fig. S39 ^{13}C NMR Spectrum of 9-bromo-1,7-bis(4-methoxyphenyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline ($CDCl_3$, 151 MHz, 298K)

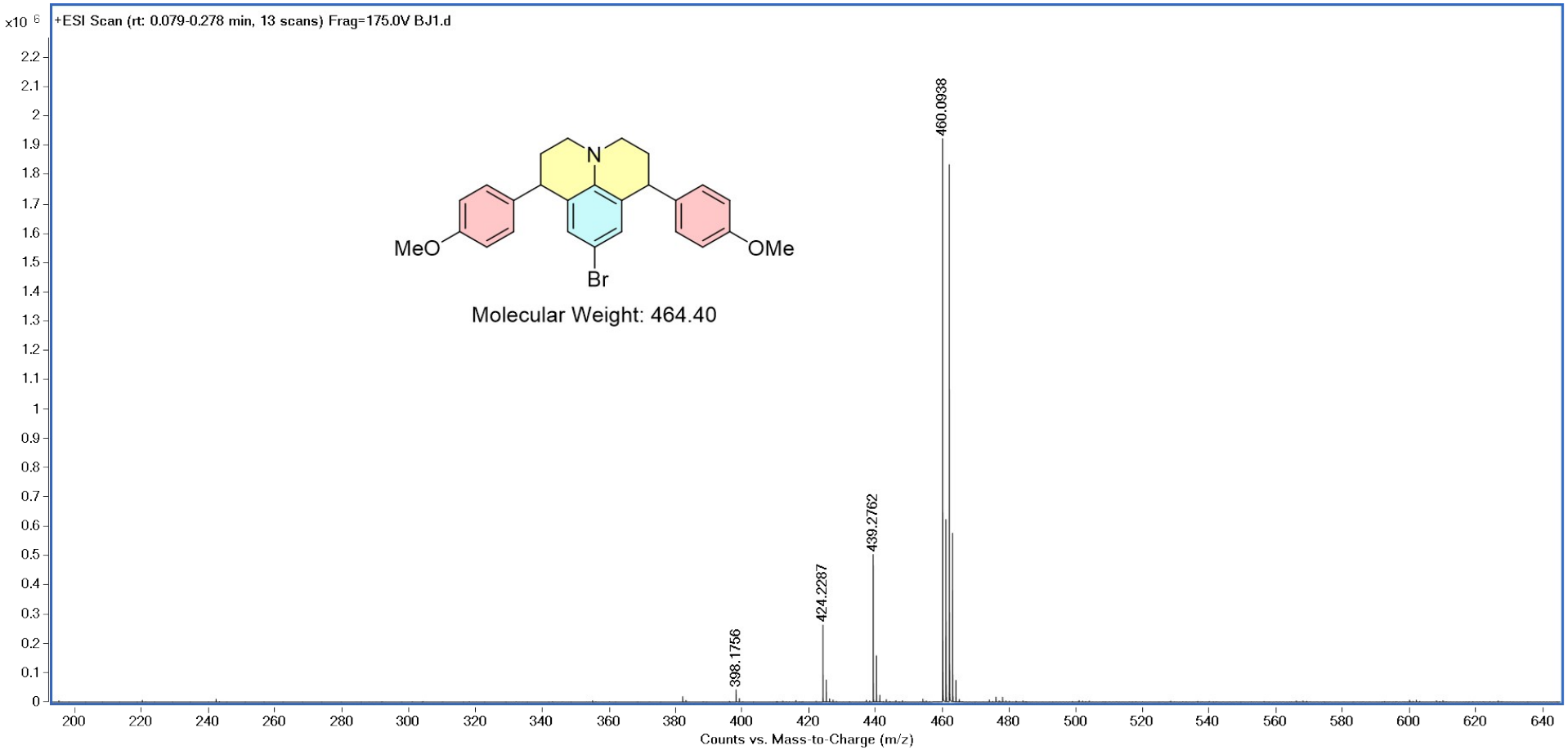


Fig. S40 ESI-MS Spectrum of 9-bromo-1,7-bis(4-methoxyphenyl)-2,6-dimethyl-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline

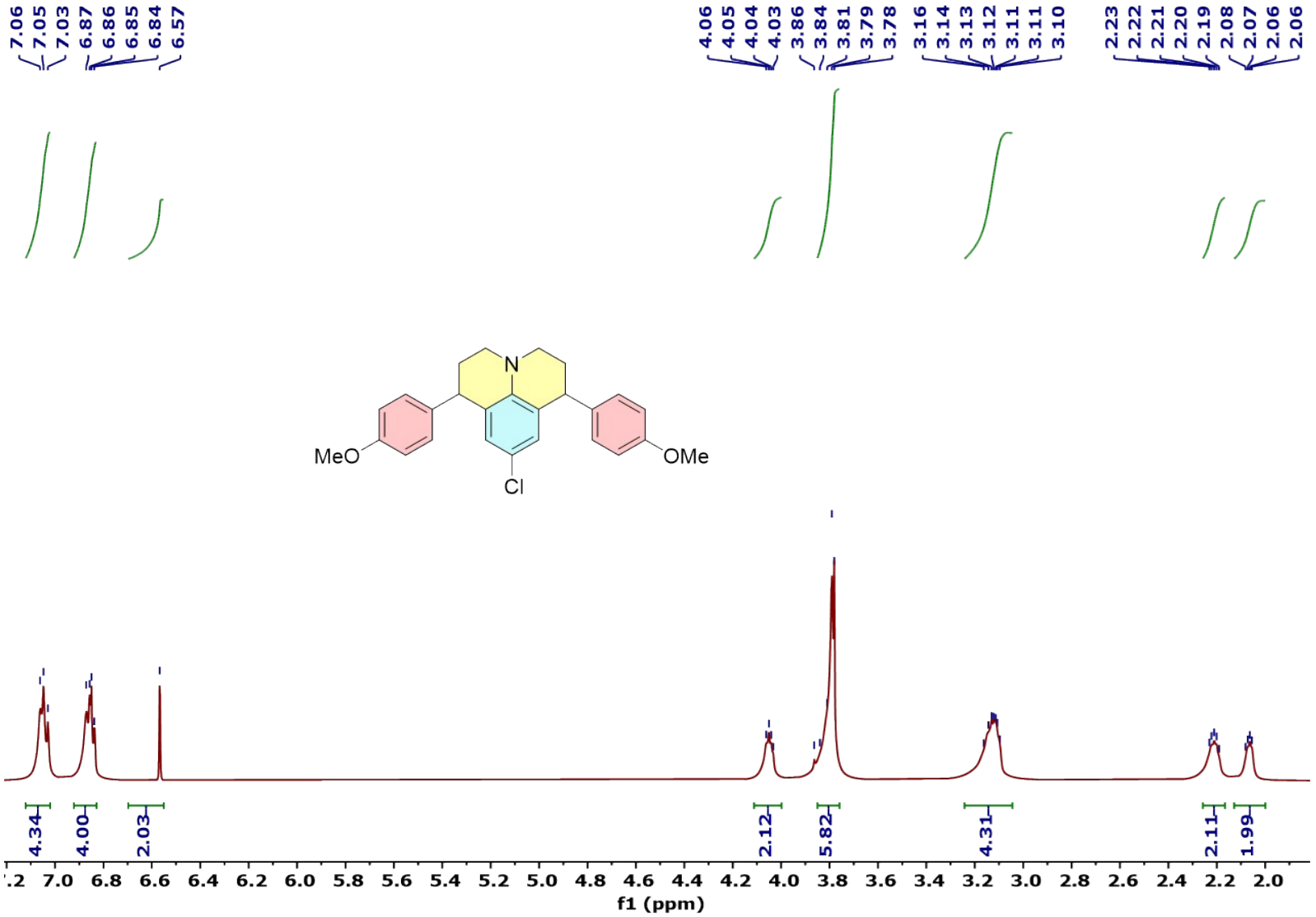


Fig. S41 ^{1}H NMR Spectrum of 9-chloro-1,7-bis(4-methoxyphenyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline ($CDCl_3$, 600 MHz, 298K)

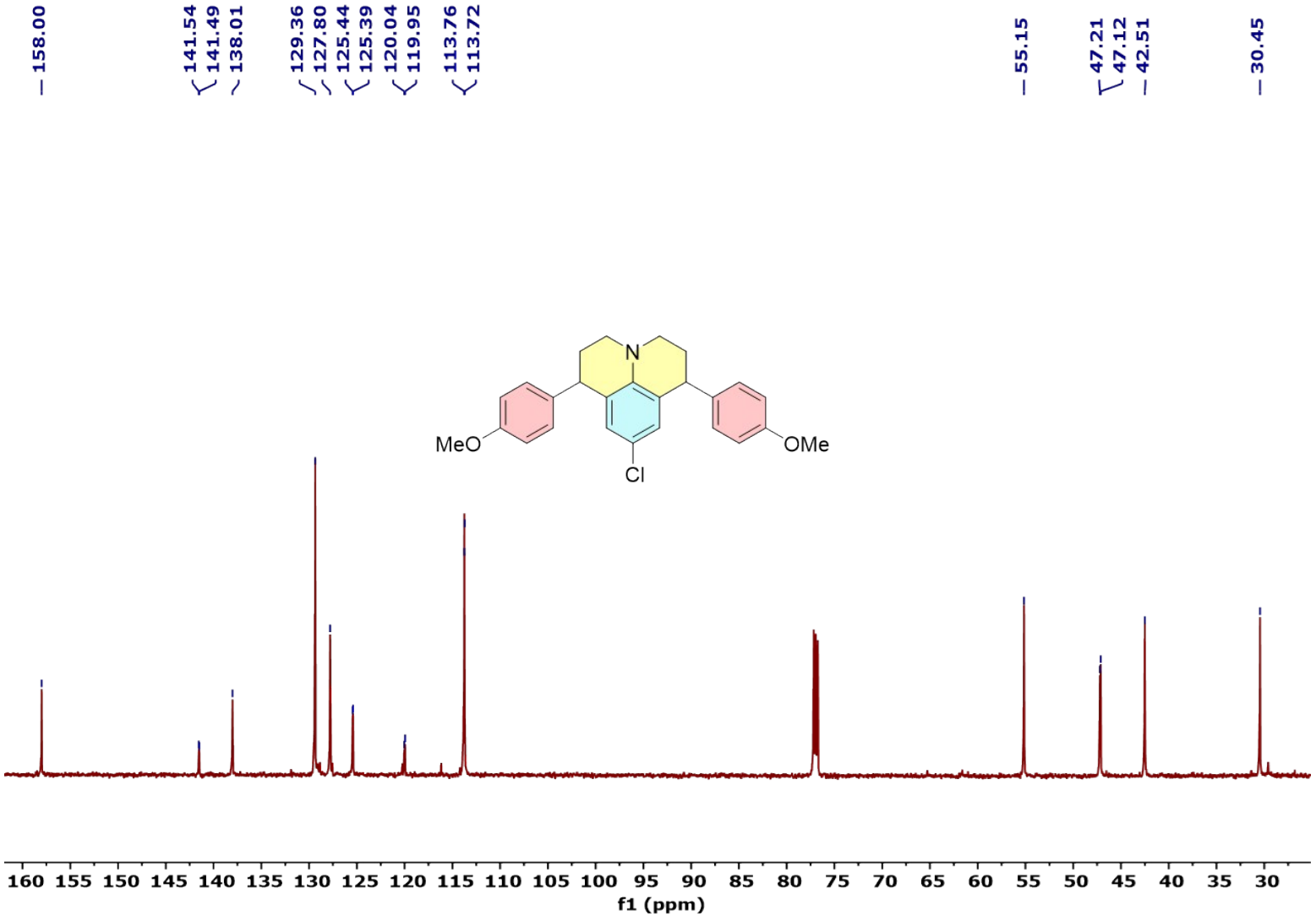


Fig. S42 ^{13}C NMR Spectrum of 9-chloro-1,7-bis(4-methoxyphenyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline $CDCl_3$, 151 MHz, 298K)

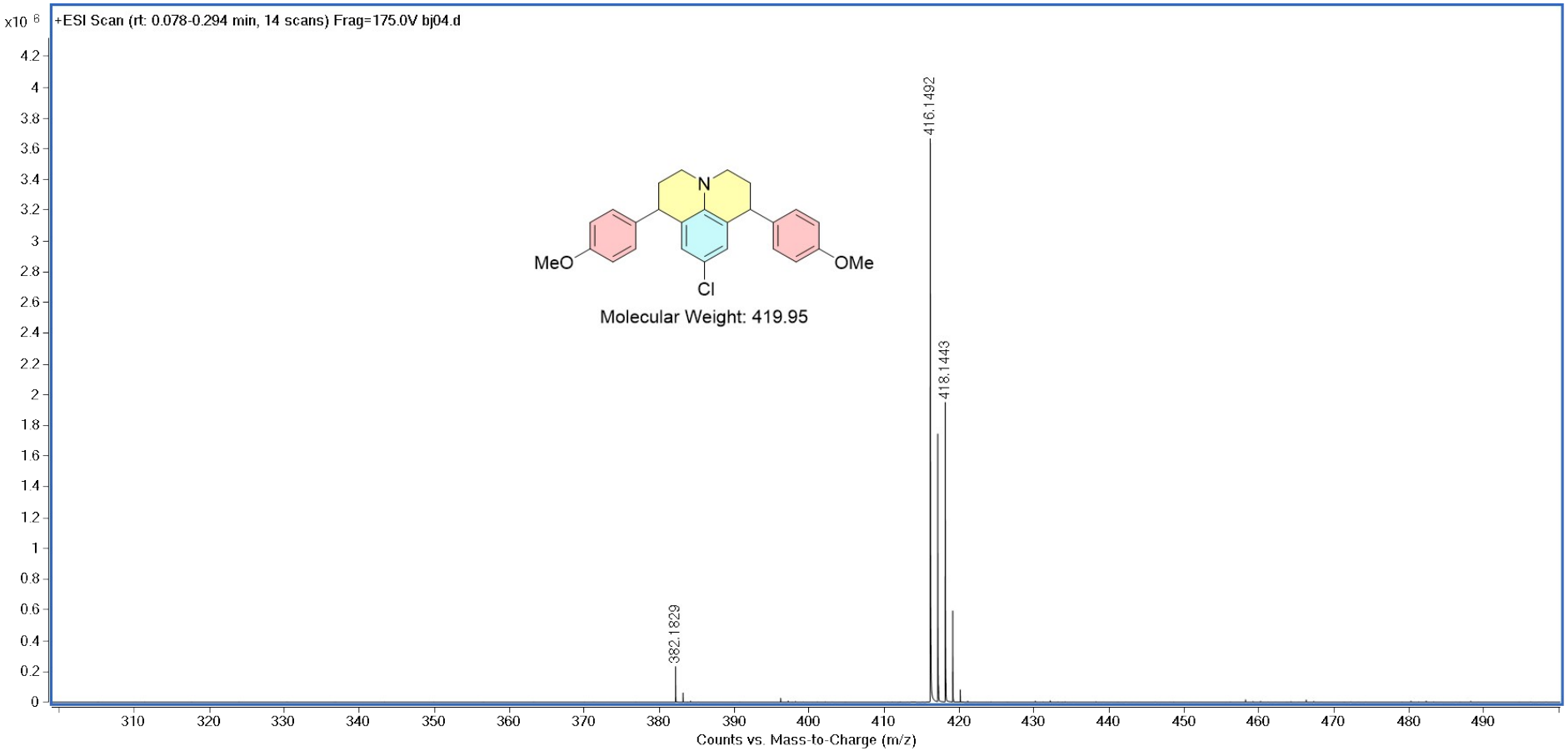


Fig. S43 ESI-MS Spectrum of 9-Chloro-1,7-bis(4-methoxyphenyl)-2,6-dimethyl-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline

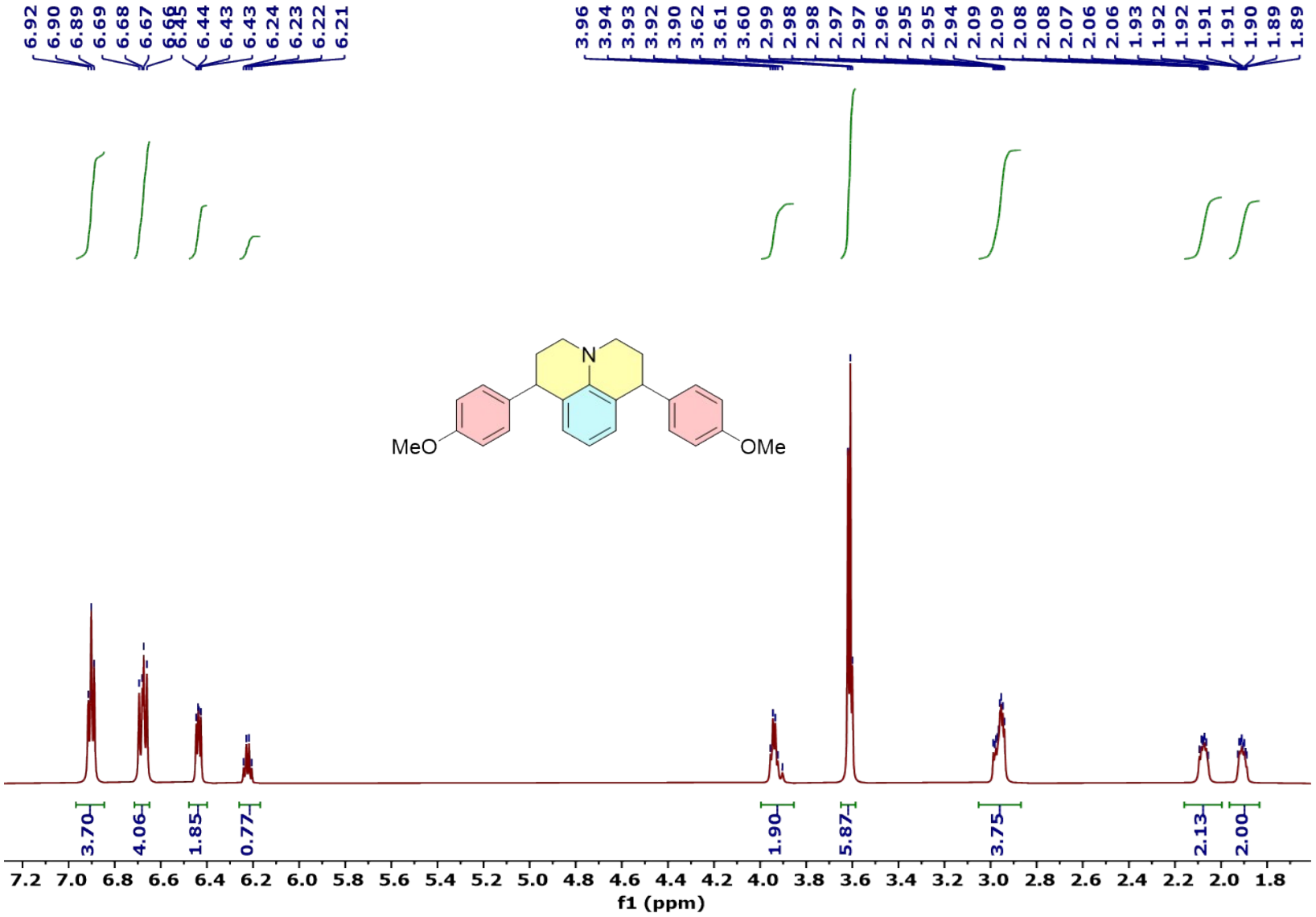


Fig. S44 ^{1}H NMR Spectrum of 11.1,7-bis(4-methoxyphenyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline ($CDCl_3$, 600 MHz, 298K)

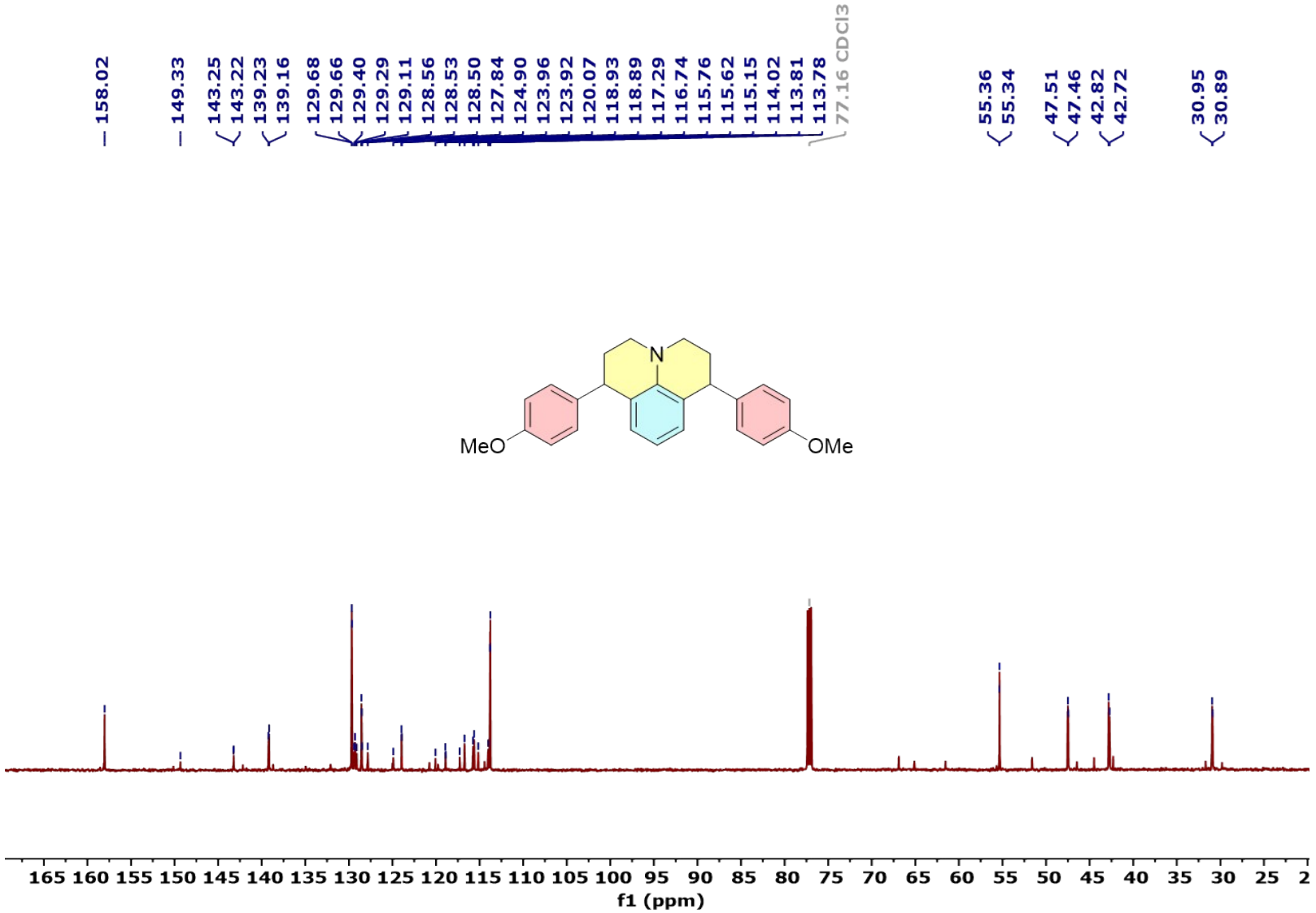


Fig. S45 ^{13}C NMR Spectrum of 1,7-bis(4-methoxyphenyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline ($CDCl_3$, 151 MHz, 298K)

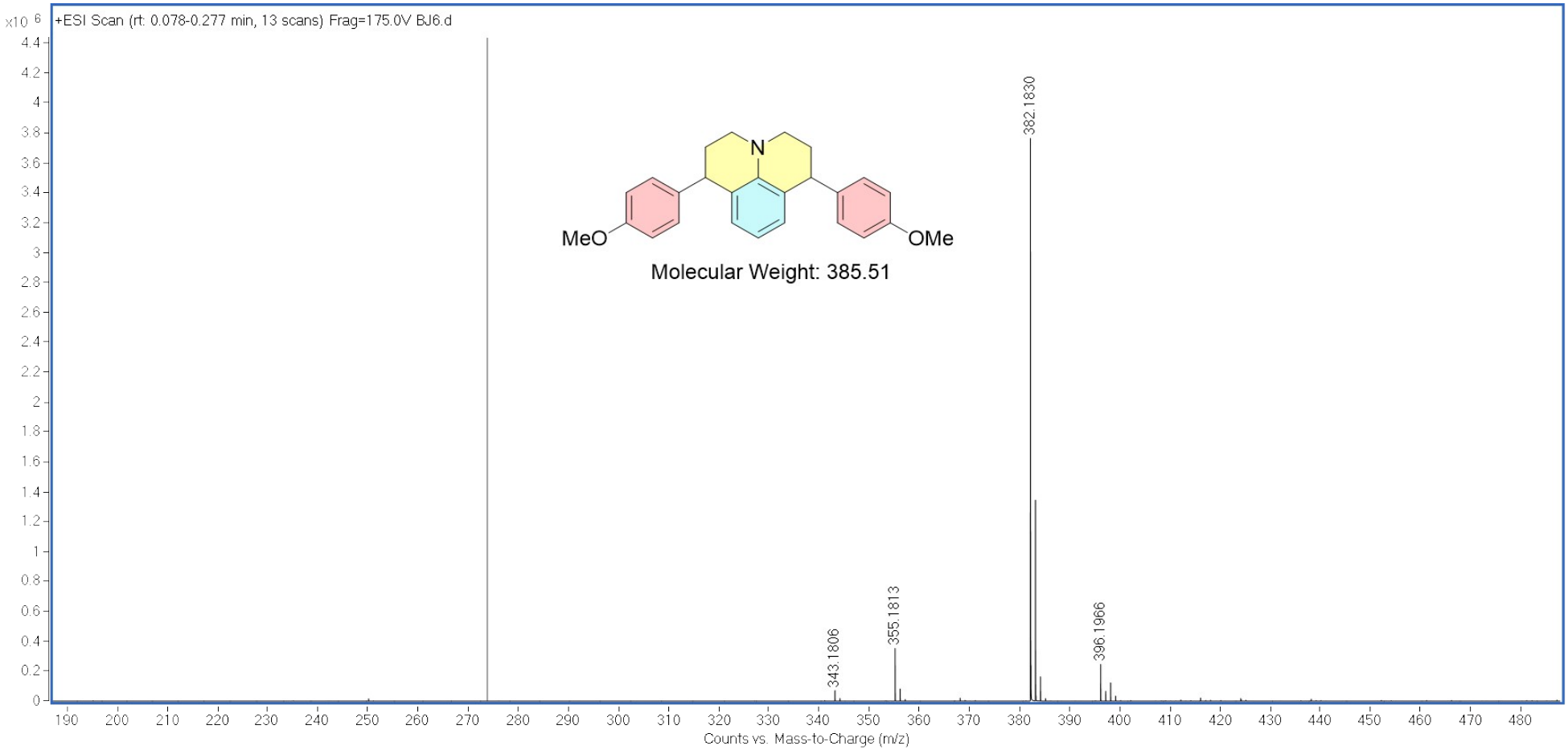


Fig. S46 ESI-MS Spectrum of 1,7-bis(4-methoxyphenyl)-2,6-dimethyl-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline

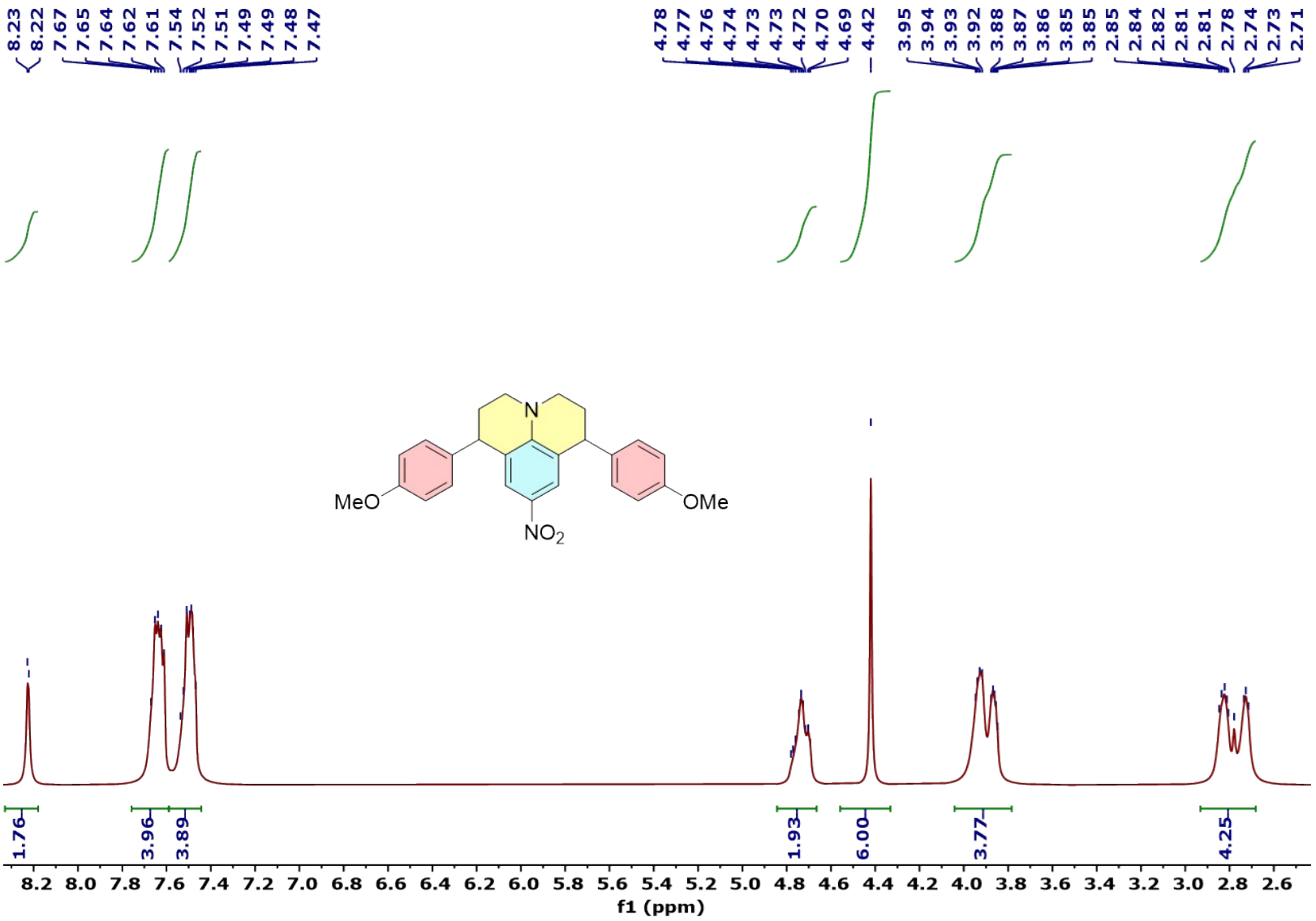


Fig. S47 ^{1}H NMR Spectrum of 1,7-bis(4-methoxyphenyl)-9-nitro-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline ($CDCl_3$, 600 MHz, 298K)

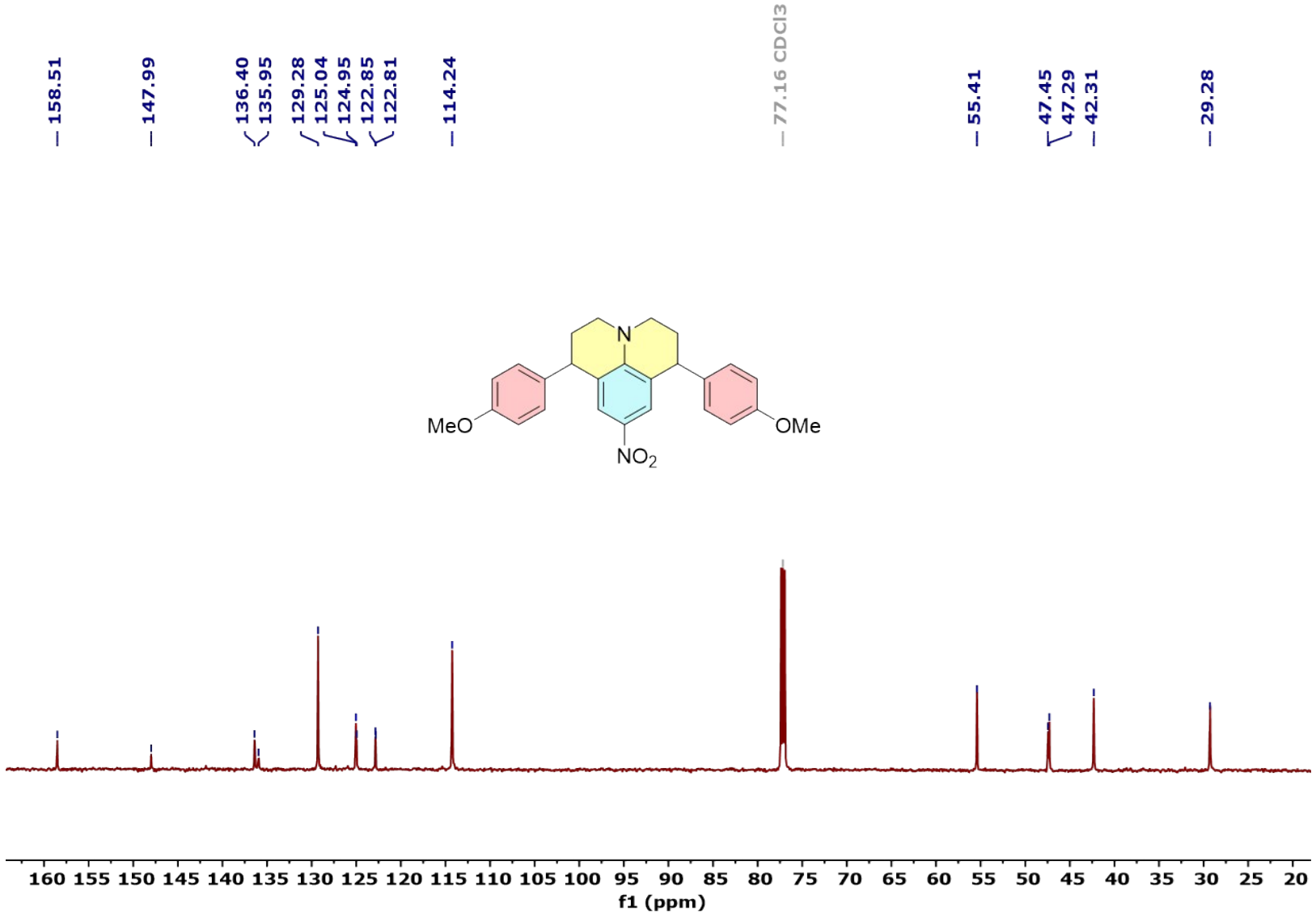


Fig. S48 ^{13}C NMR Spectrum of 1,7-bis(4-methoxyphenyl)-9-nitro-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline ($CDCl_3$, 151 MHz, 298K)

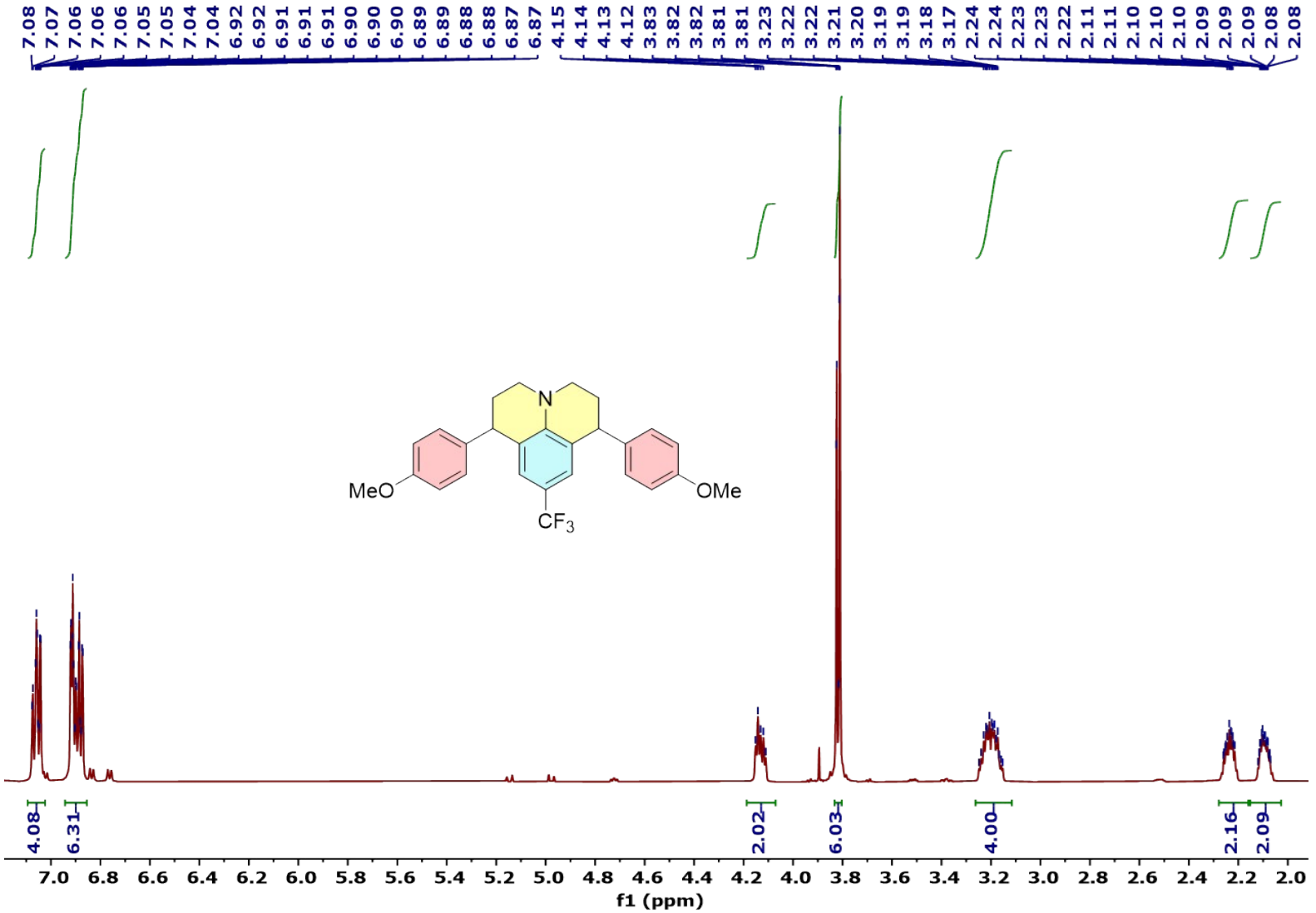


Fig. S49 ^{1}H NMR Spectrum of 1,7-bis(4-methoxyphenyl)-9-(trifluoromethyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline ($CDCl_3$, 600 MHz, 298K)

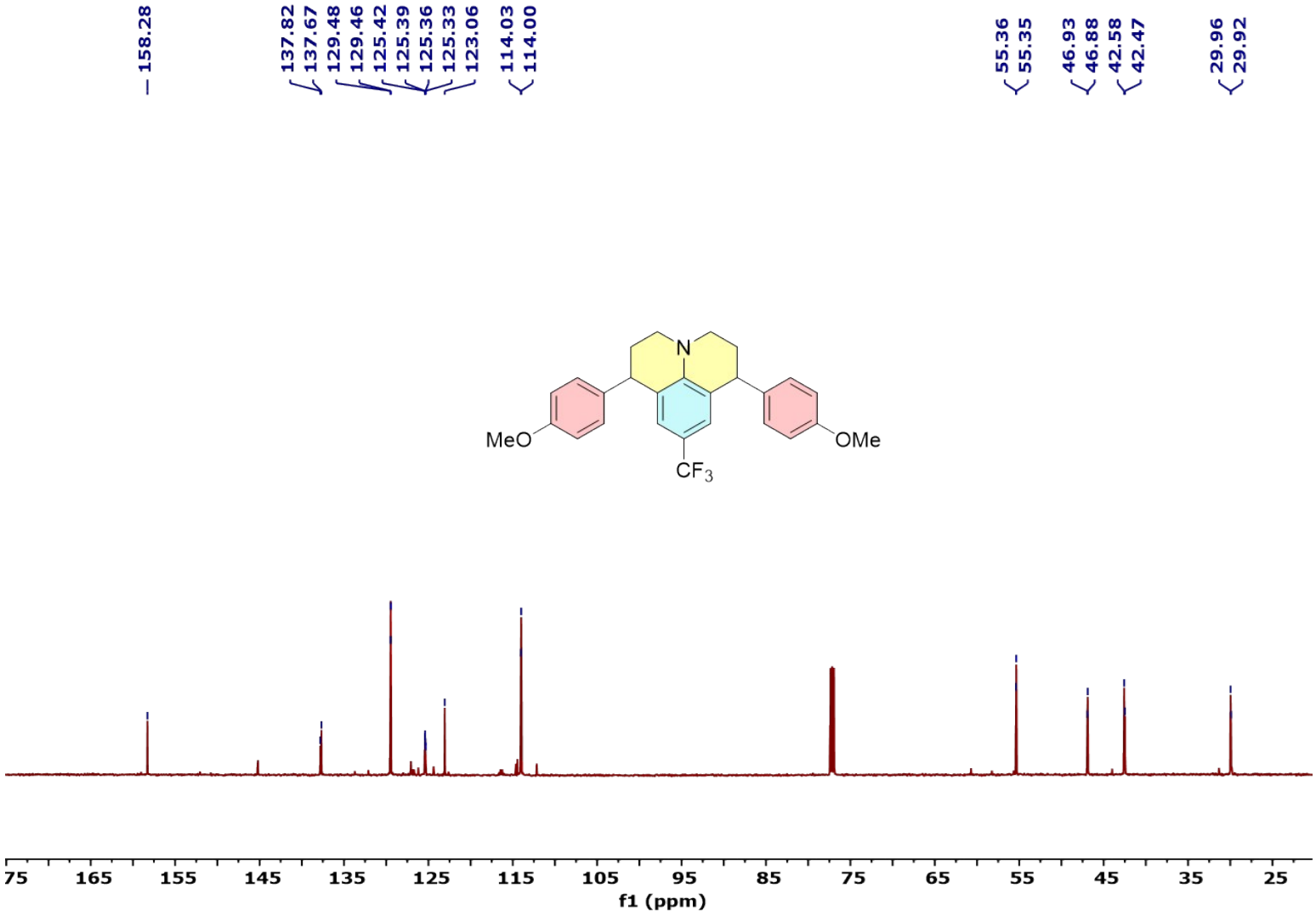


Fig. S50 ^{13}C NMR Spectrum of 1,7-bis(4-methoxyphenyl)-9-(trifluoromethyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline ($CDCl_3$, 151 MHz, 298K)

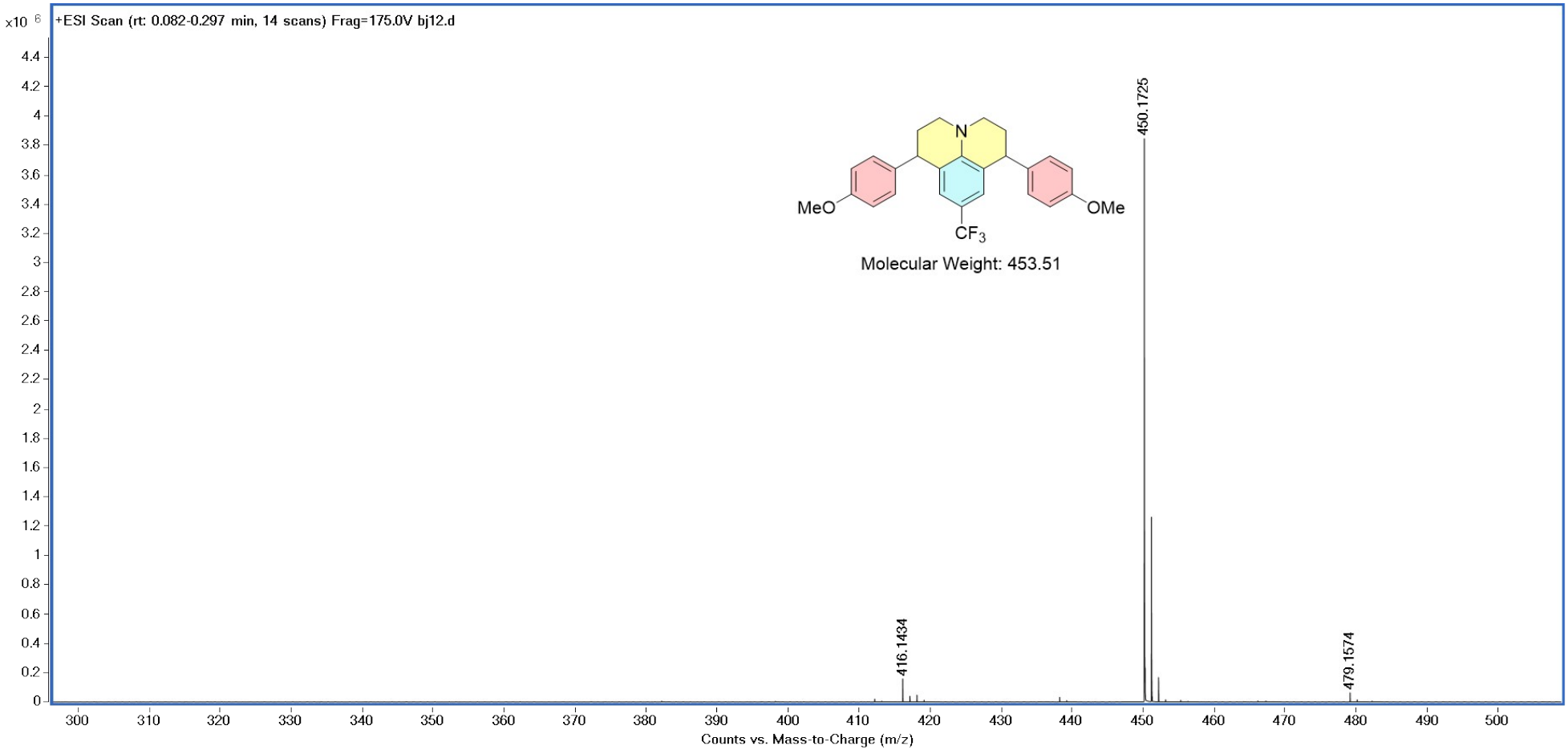


Fig. S51 ESI-MS Spectrum of 1,7-bis(4-methoxyphenyl)-9-(trifluoromethyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline

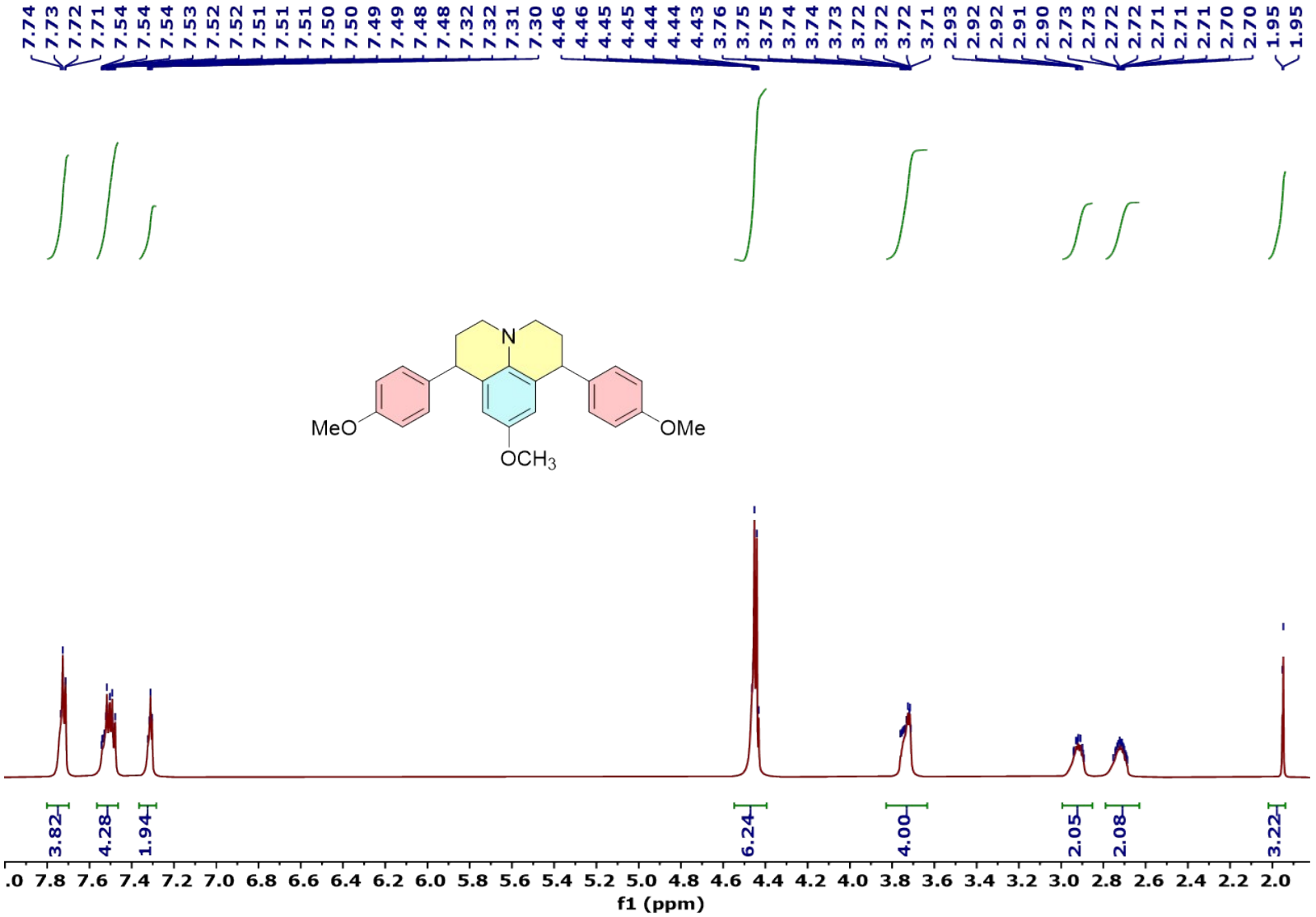


Fig. S52 ^{1}H NMR Spectrum of 9-methoxy-1,7-bis(4-methoxyphenyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline ($CDCl_3$, 600 MHz, 298K)

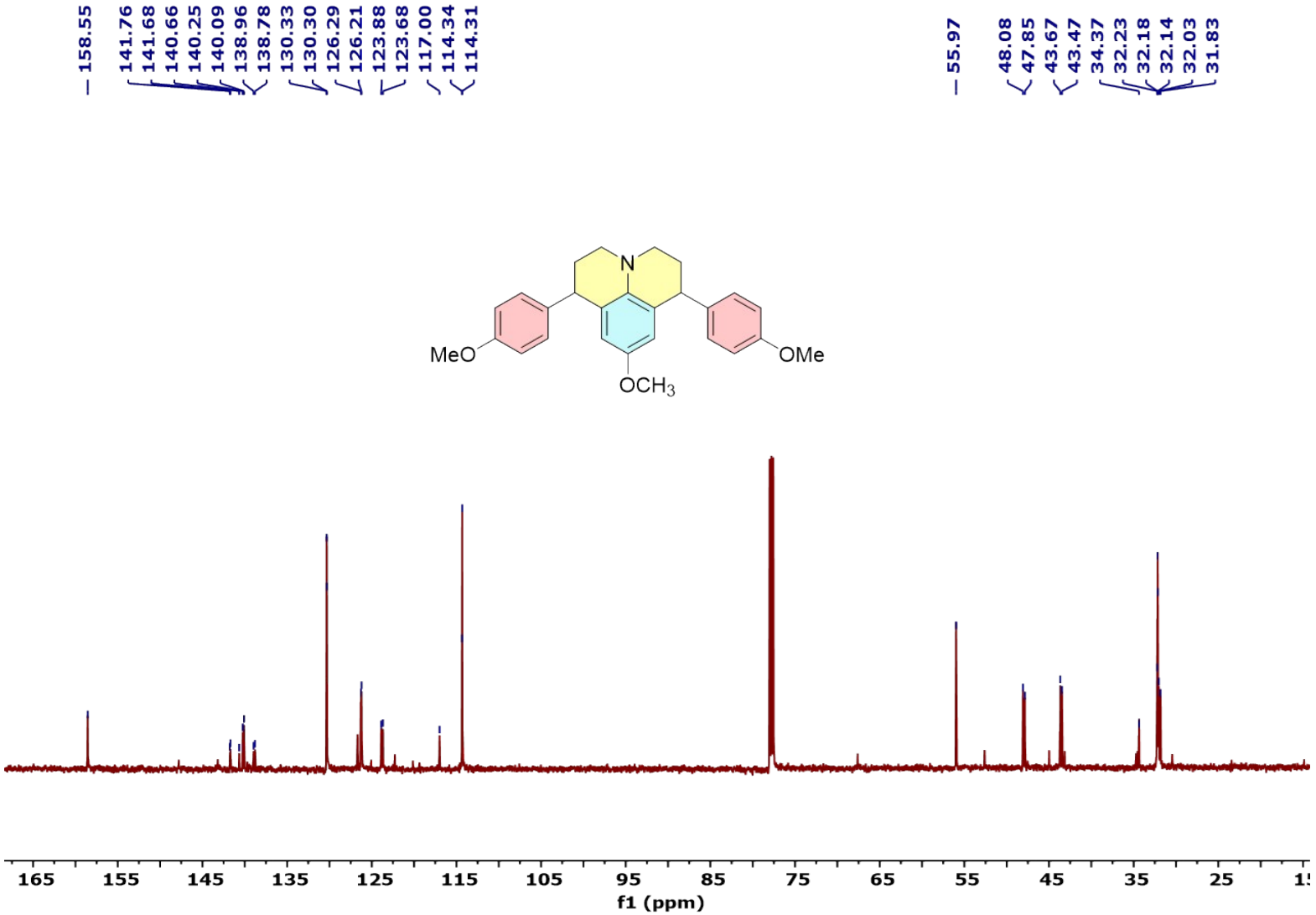


Fig. S53 ^{13}C NMR Spectrum of 9-methoxy-1,7-bis(4-methoxyphenyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline ($CDCl_3$, 151 MHz, 298K)

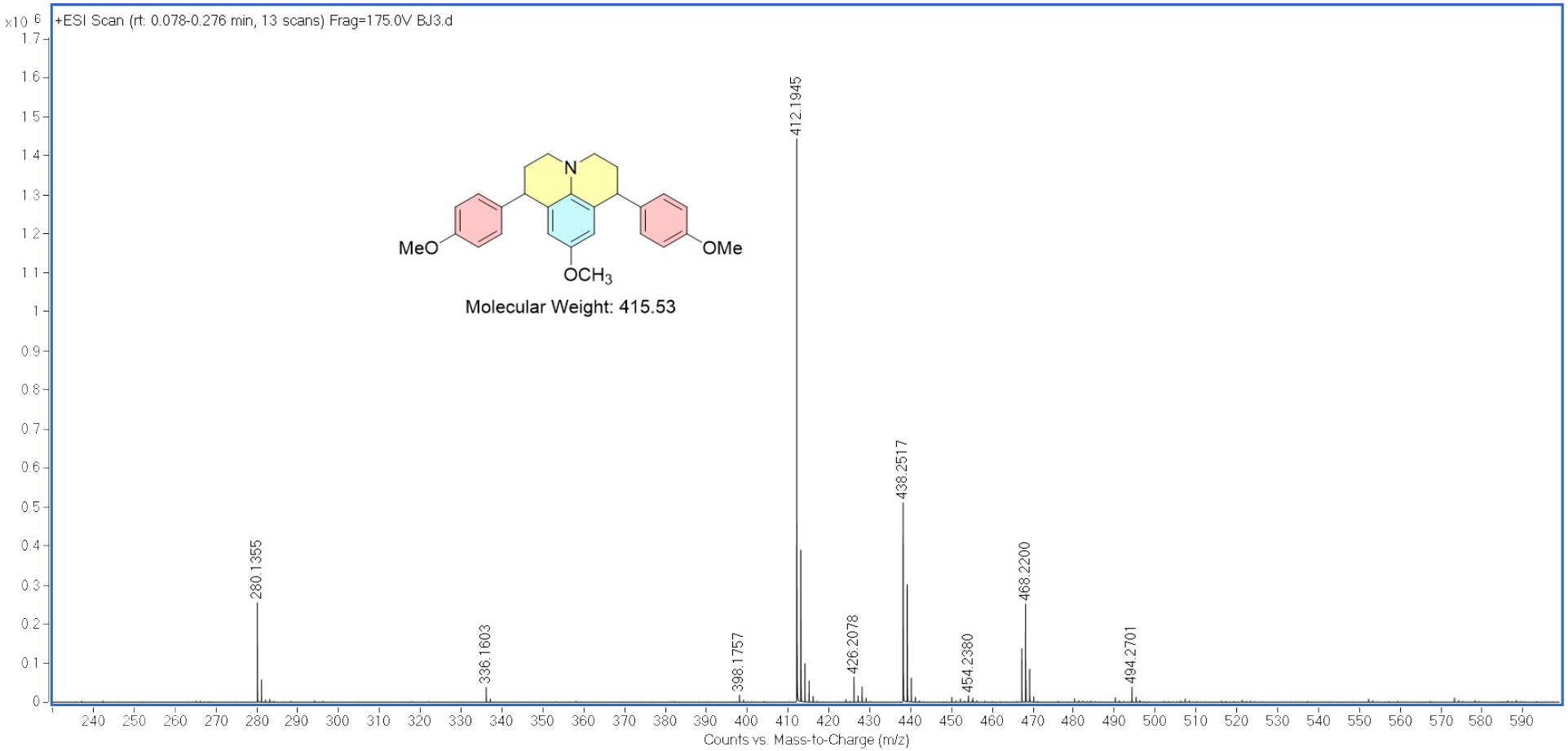


Fig. S54 ESI-MS Spectrum of 9-methoxy-1,7-bis(4-methoxyphenyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline

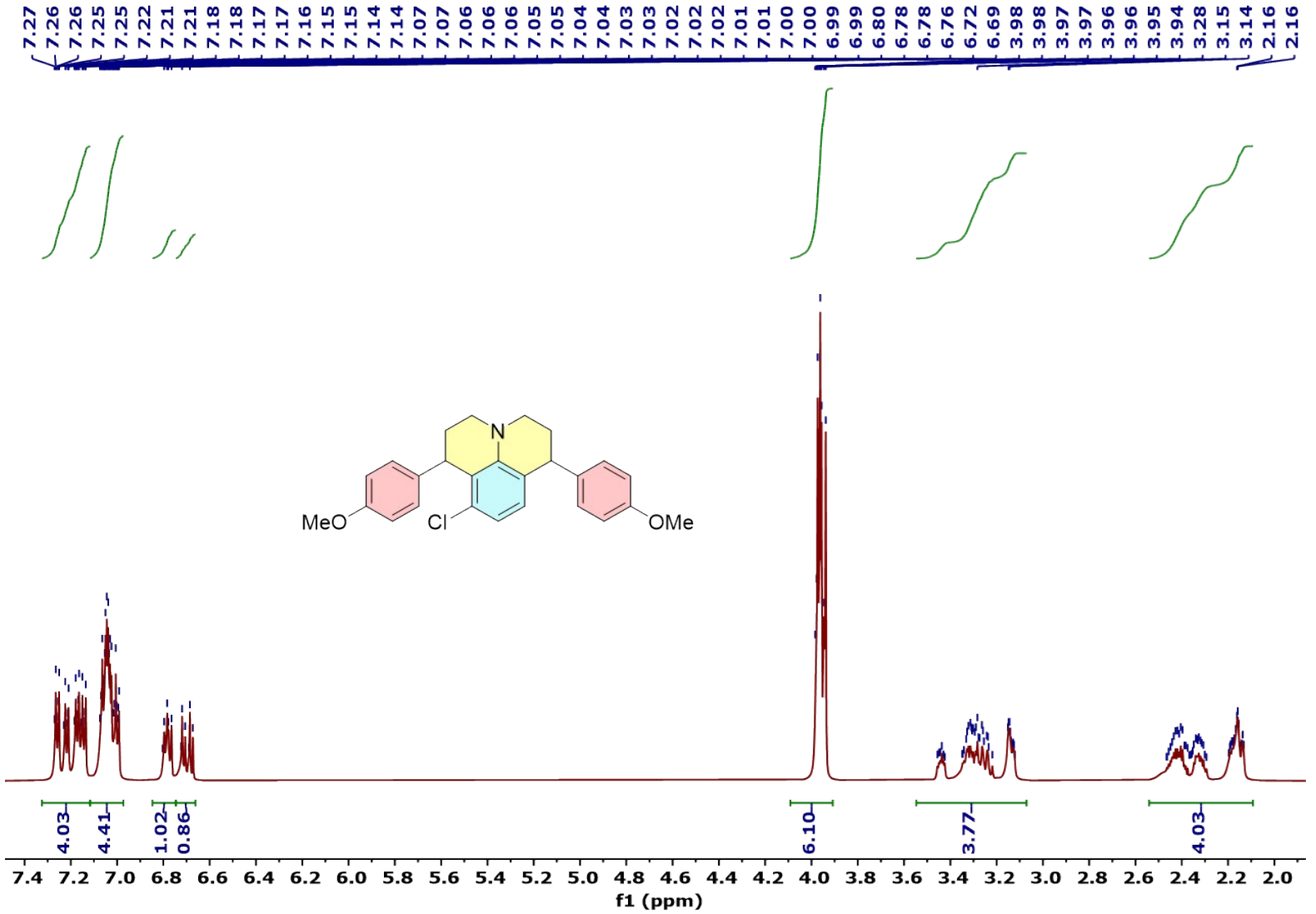


Fig. S55 ^{1}H NMR Spectrum of 8-chloro-1,7-bis(4-methoxyphenyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline ($CDCl_3$, 600 MHz, 298K)

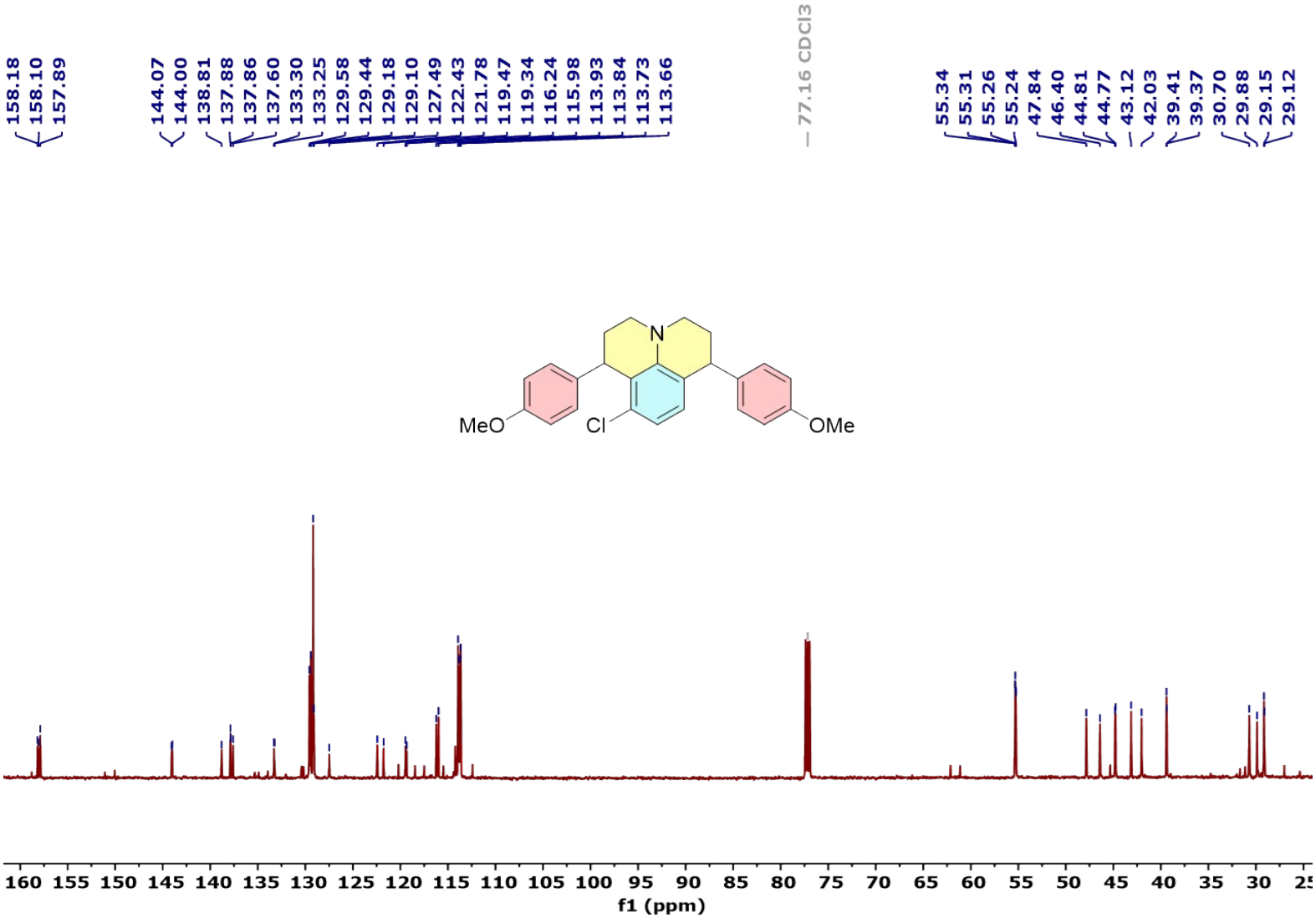


Fig. S56 ^{13}C NMR Spectrum of 8-chloro-1,7-bis(4-methoxyphenyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline ($CDCl_3$, 151 MHz, 298K)

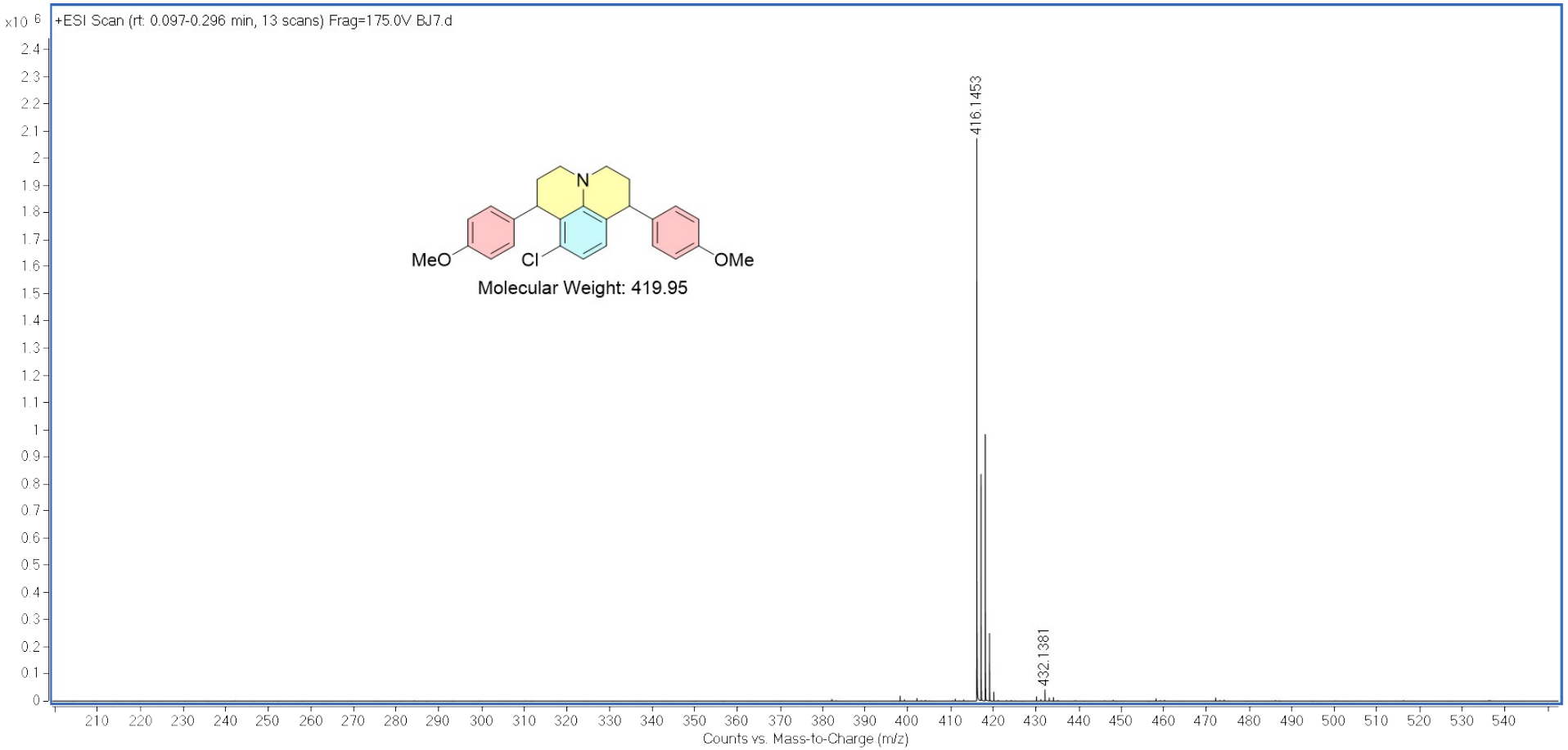


Fig. S57 ESI-MS Spectrum of 8-chloro-1,7-bis(4-methoxyphenyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline

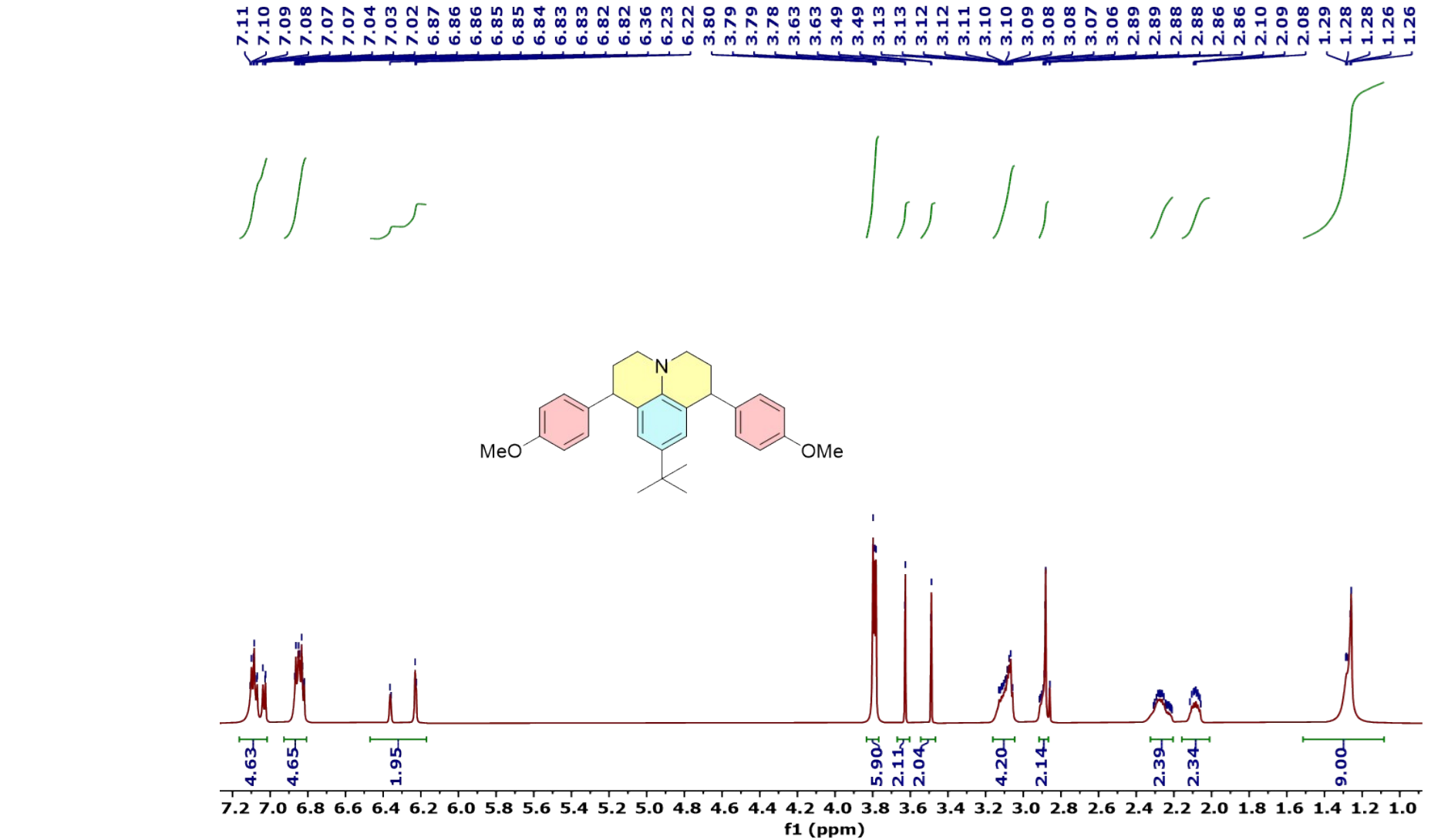


Fig. S58 ^{1}H NMR Spectrum of 9-(tert-butyl)-1,7-bis(4-methoxyphenyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline ($CDCl_3$, 600 MHz, 298K)

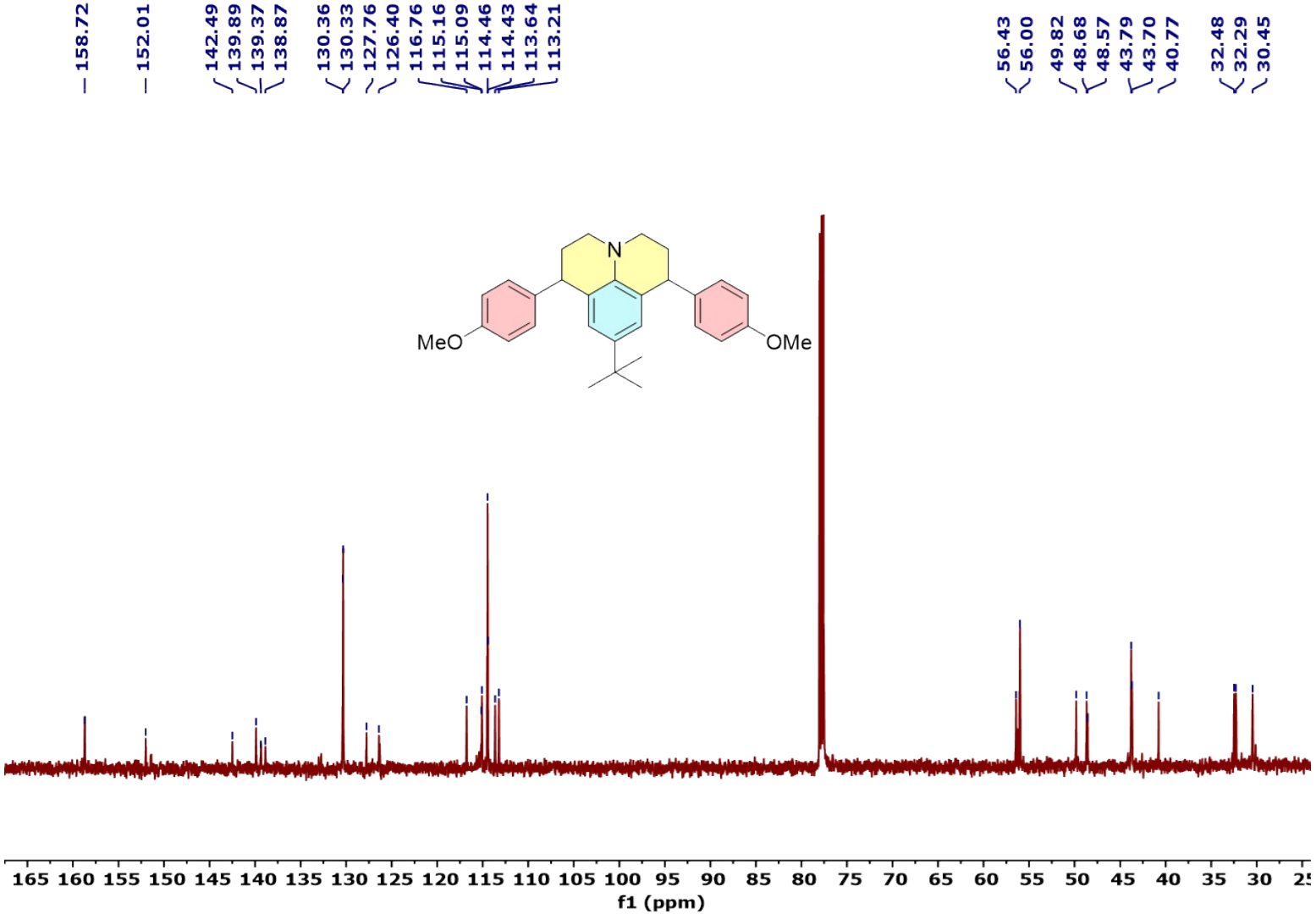


Fig. S59 ^{13}C NMR Spectrum of 9-(tert-butyl)-1,7-bis(4-methoxyphenyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline ($CDCl_3$, 151 MHz, 298K)

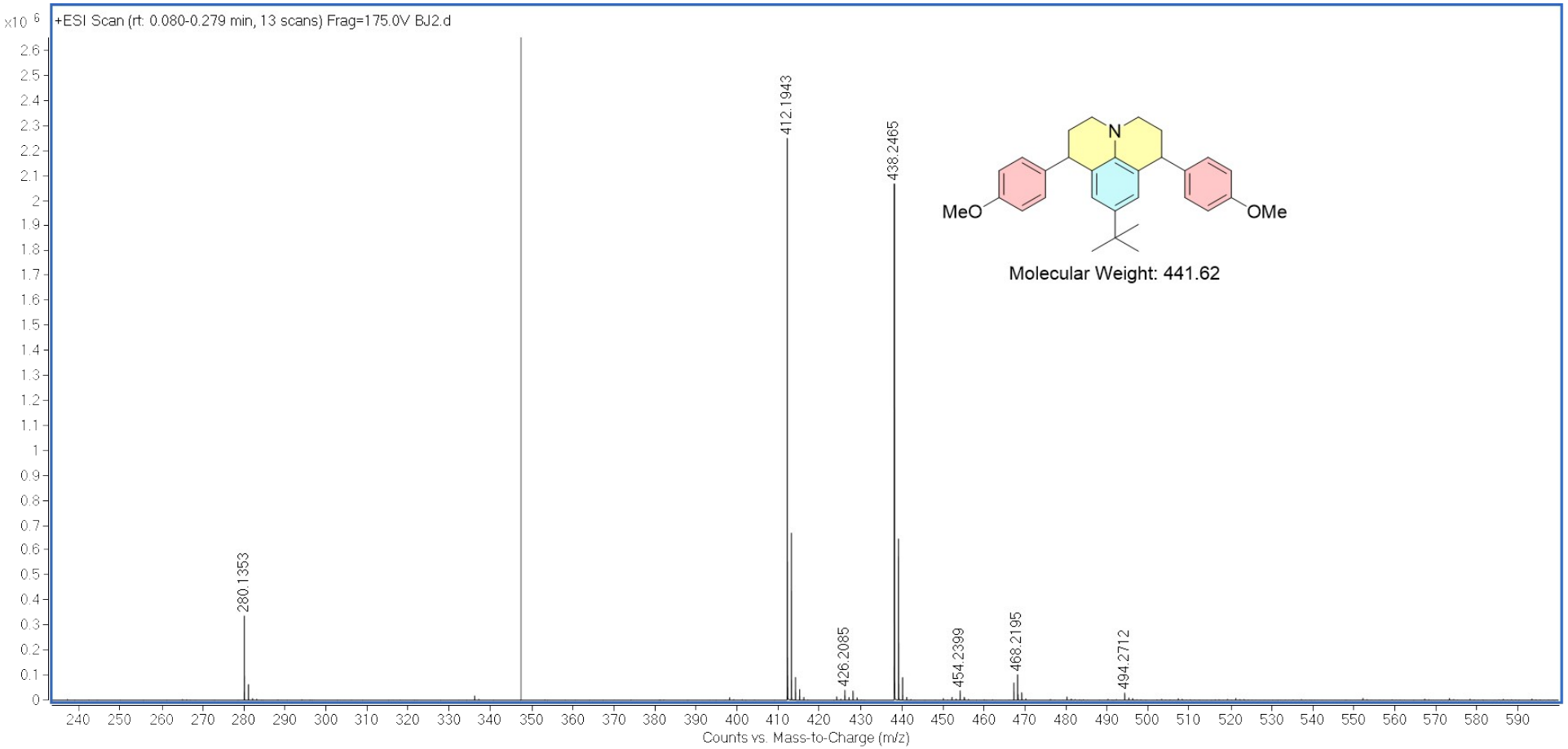


Fig. S60 ESI-MS Spectrum of 9-(tert-butyl)-1,7-bis(4-methoxyphenyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline

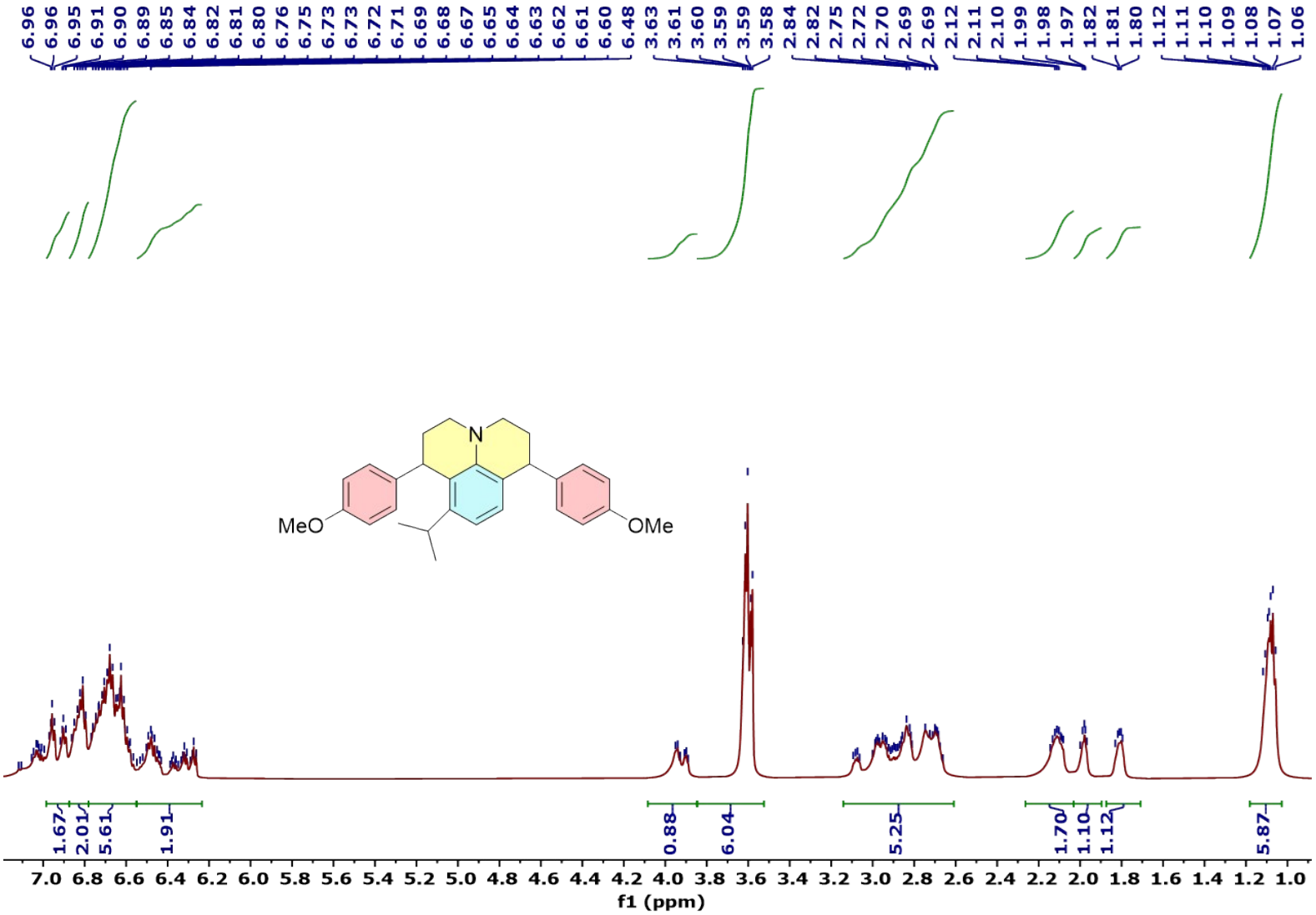


Fig. S61 ^{1}H NMR Spectrum of 8-isopropyl-1,7-bis(4-methoxyphenyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline ($CDCl_3$, 600 MHz, 298K)

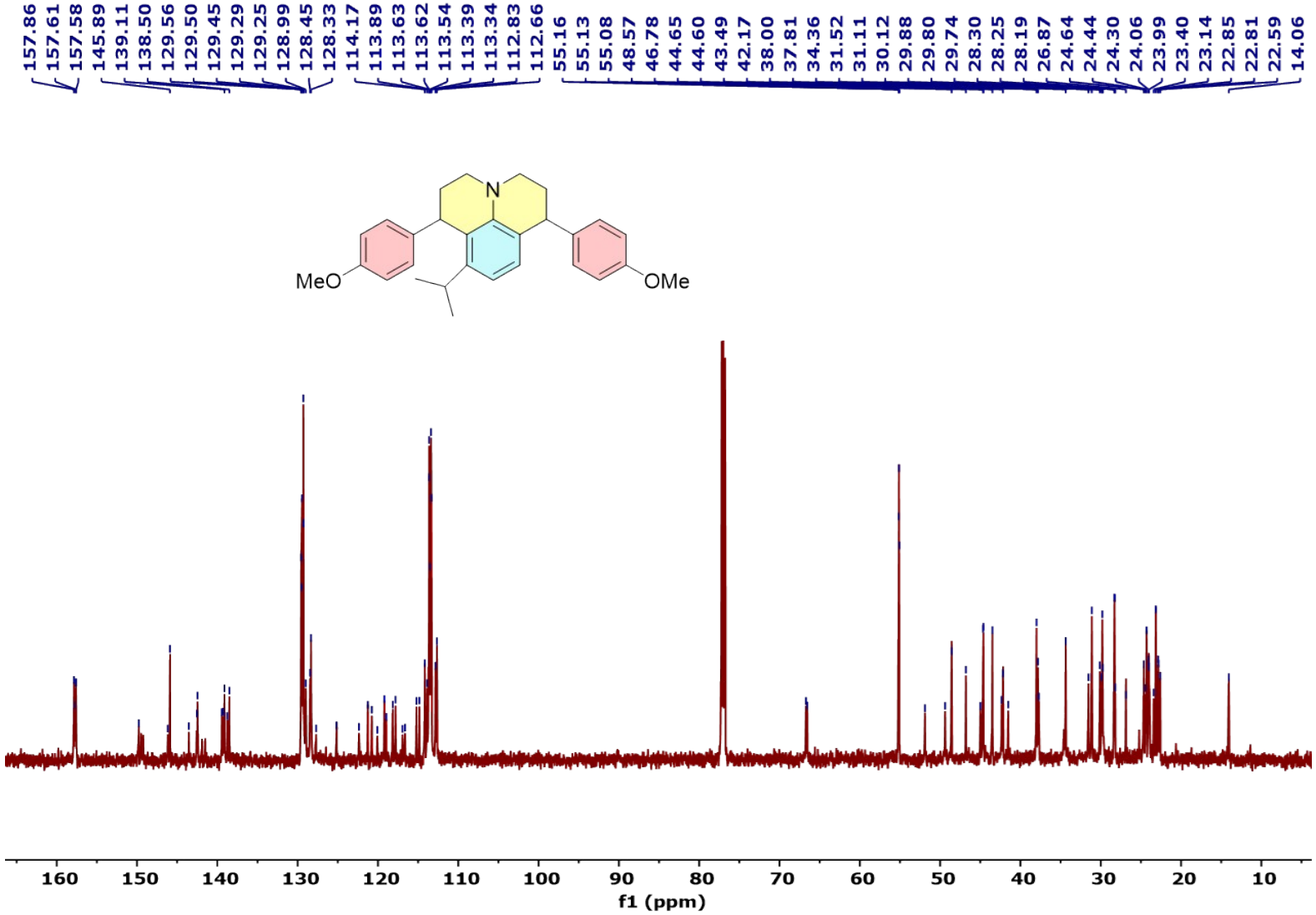


Fig. S62 ^{13}C NMR Spectrum of 8-isopropyl-1,7-bis(4-methoxyphenyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline ($CDCl_3$, 151 MHz, 298K)

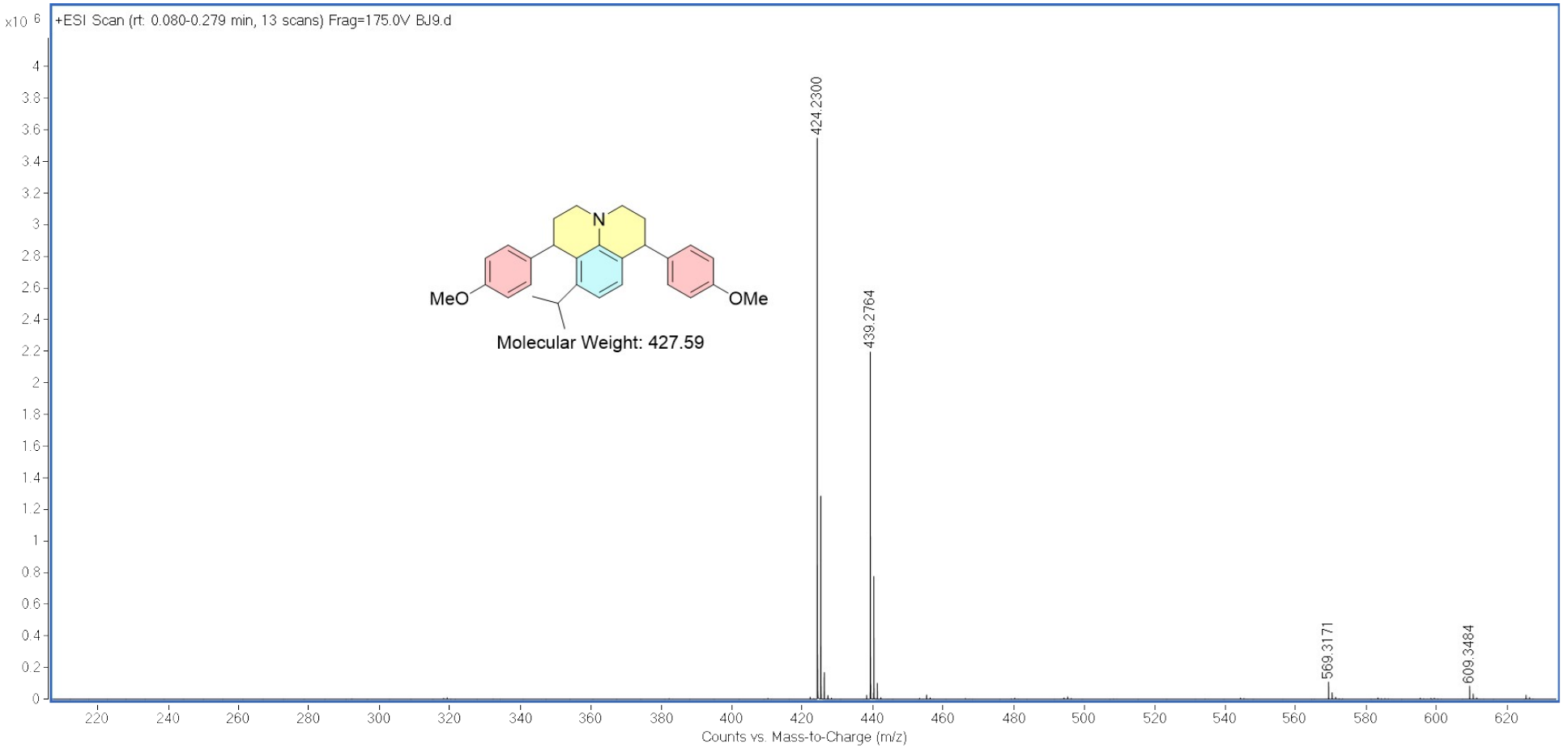


Fig. S63 ESI-MS Spectrum of 8-isopropyl-1,7-bis(4-methoxyphenyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline

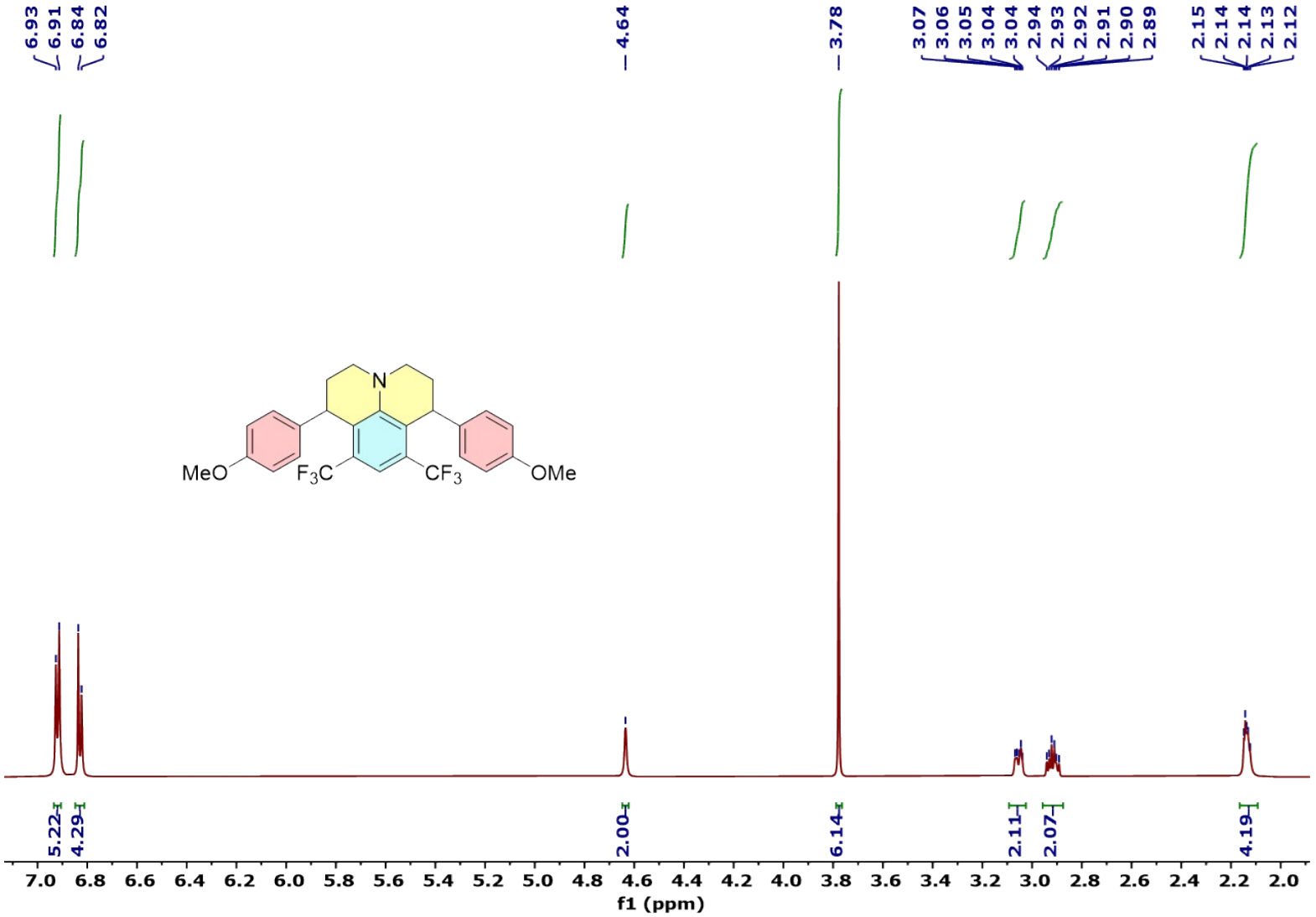


Fig. S64 ^{1}H NMR Spectrum of 1,7-bis(4-methoxyphenyl)-8,10-bis(trifluoromethyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline ($CDCl_3$, 600 MHz, 298K)

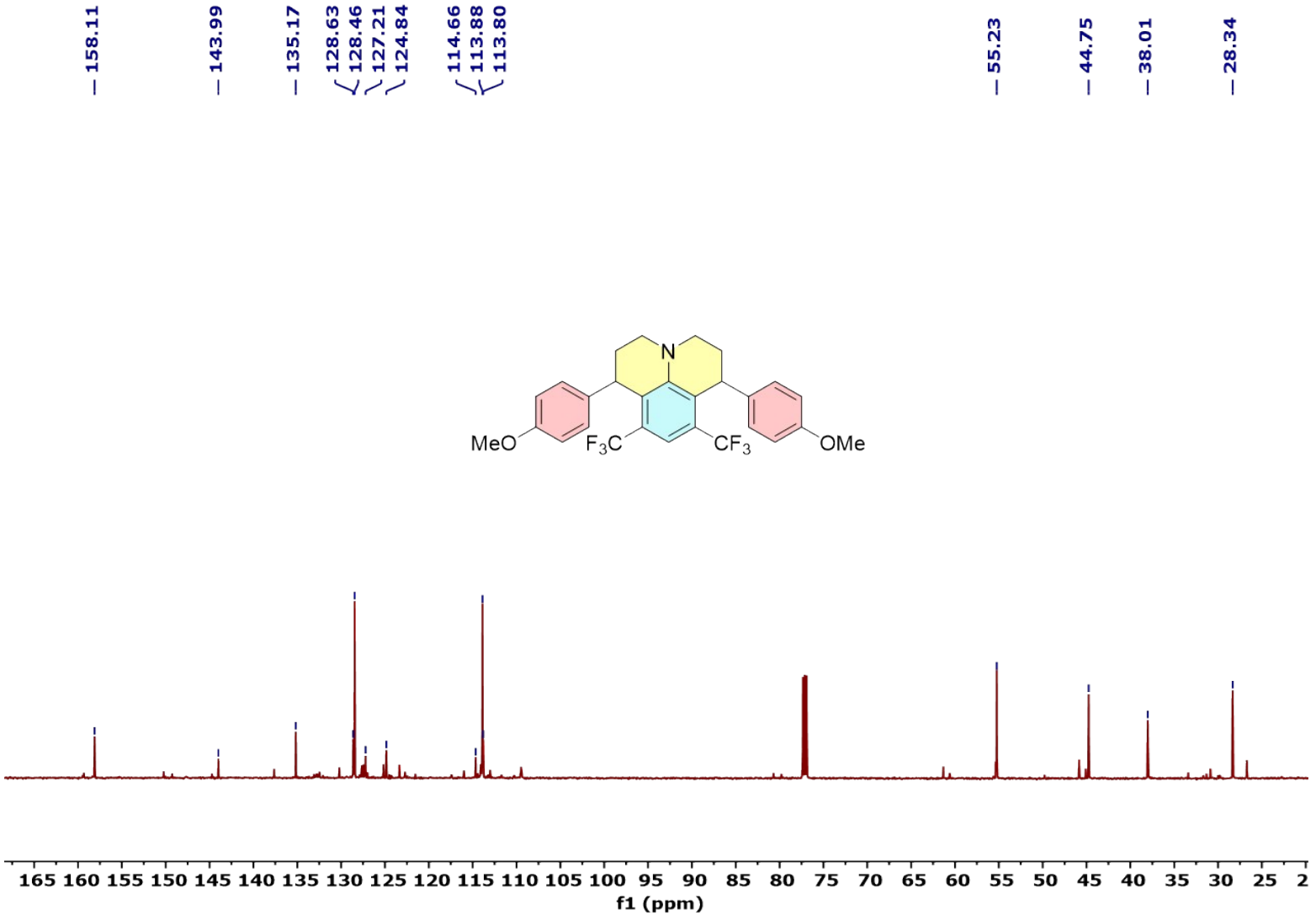


Fig. S65 ^{13}C NMR Spectrum of 1,7-bis(4-methoxyphenyl)-8,10-bis(trifluoromethyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline ($CDCl_3$, 151 MHz, 298K)

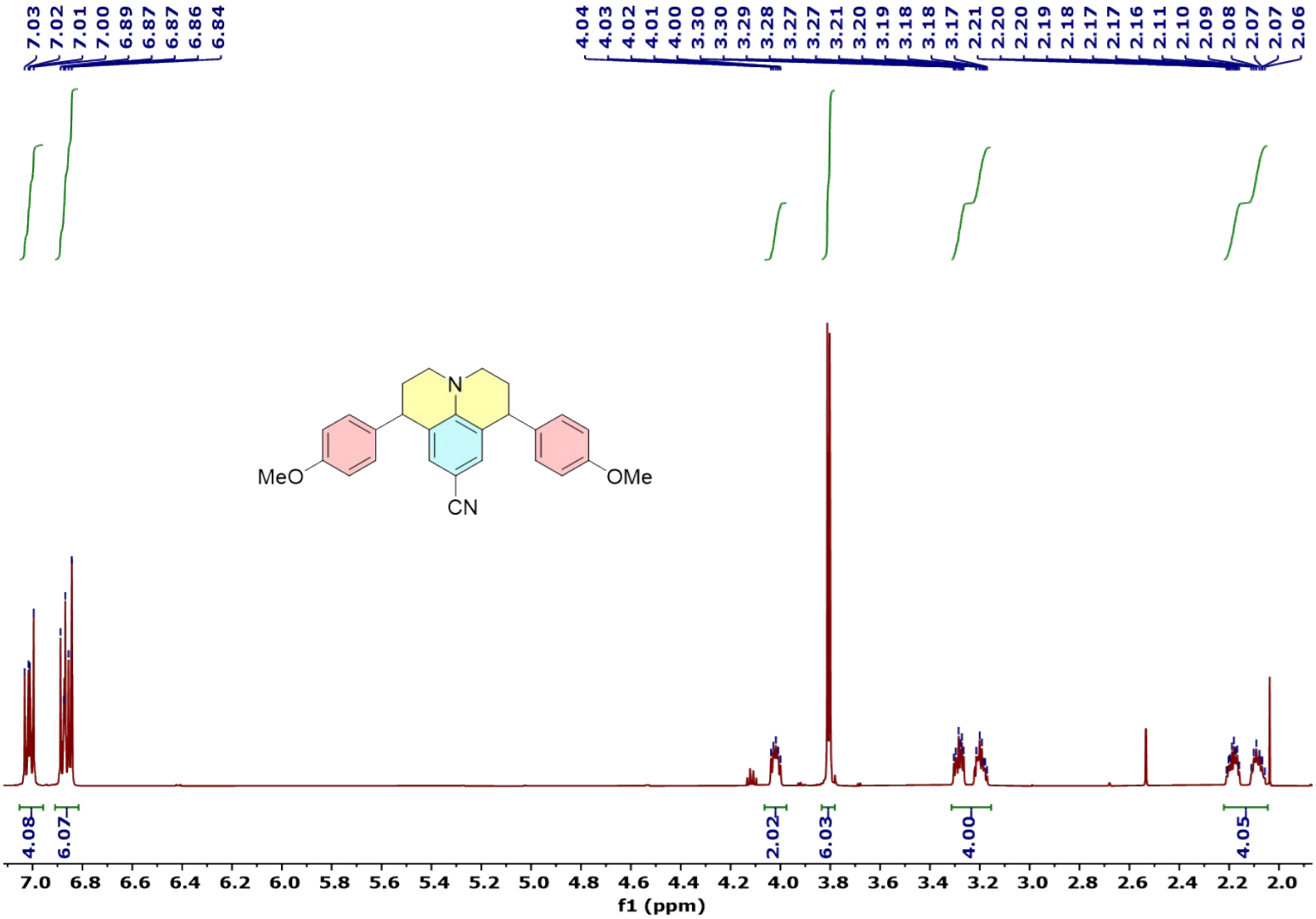


Fig. S66 ^{1}H NMR Spectrum of 1,7-bis(4-methoxyphenyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline-9-carbonitrile ($CDCl_3$, 600 MHz, 298K)

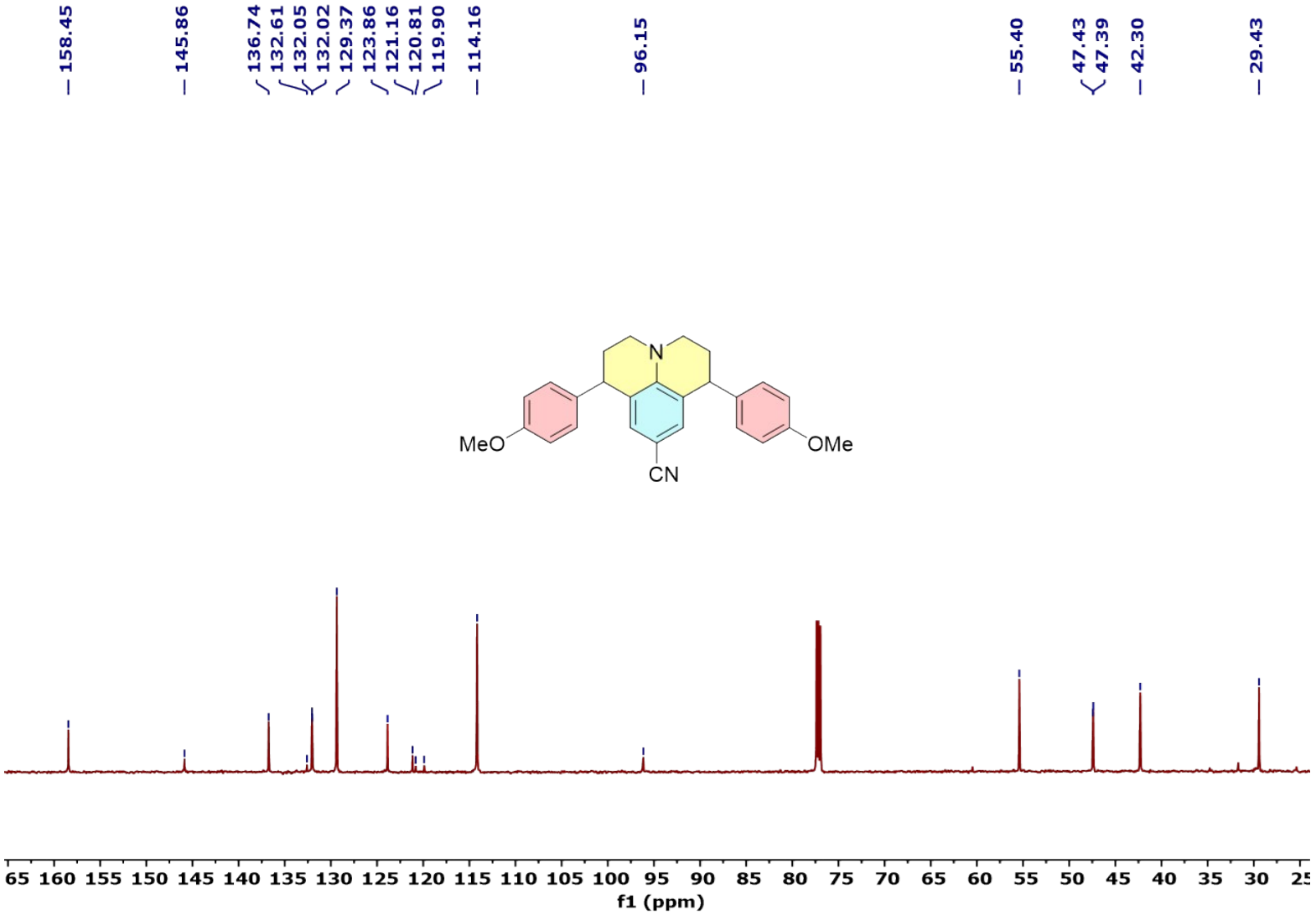


Fig. S67 ^{13}C NMR Spectrum of 1,7-bis(4-methoxyphenyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline-9-carbonitrile ($CDCl_3$, 151MHz, 298K)

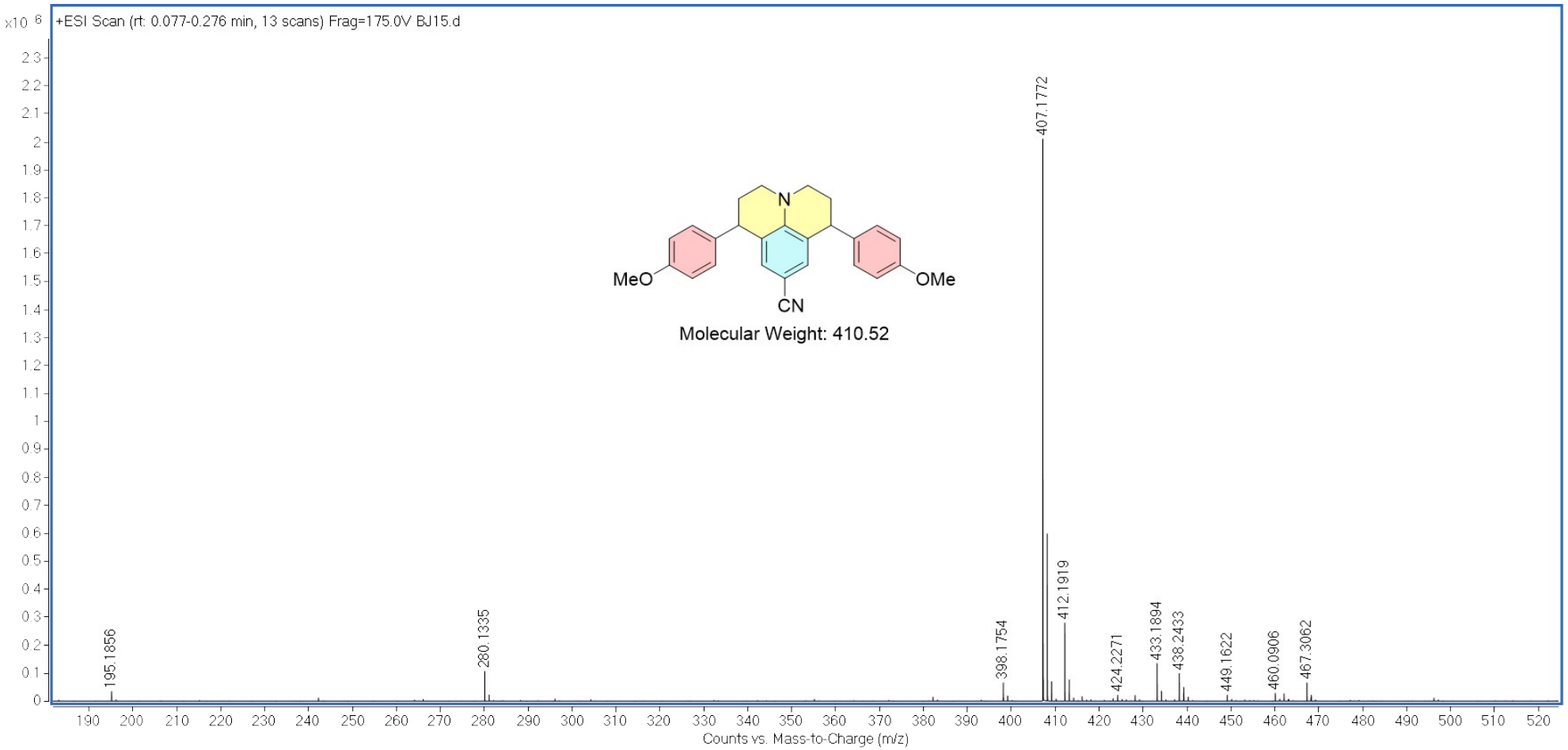


Fig. S69 ESI-MS Spectrum of 1,7-bis(4-methoxyphenyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline-9-carbonitrile

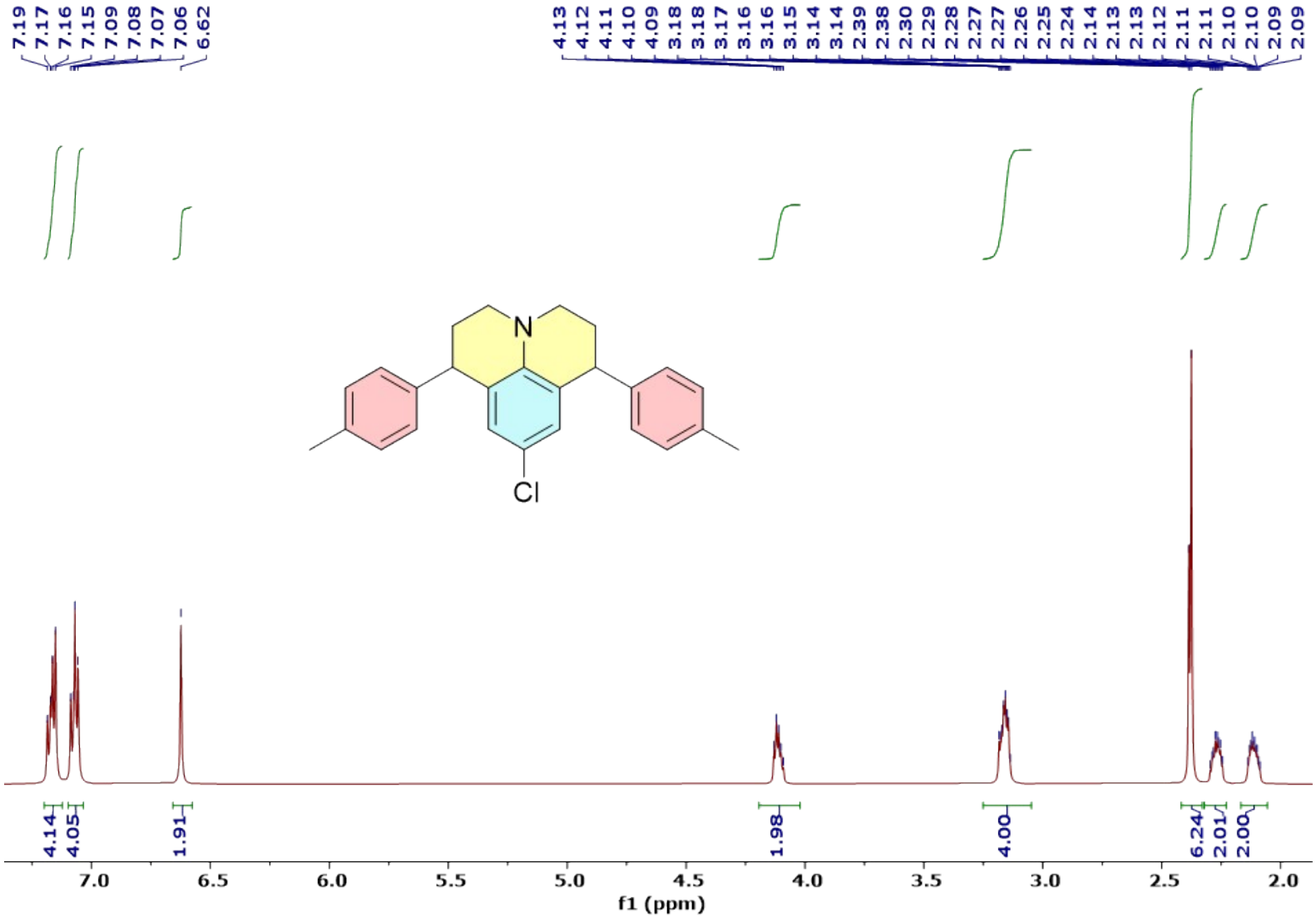


Fig. S70 ^{1}H NMR Spectrum of 9-chloro-1,7-di-p-tolyl-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline ($CDCl_3$, 600 MHz, 298K)

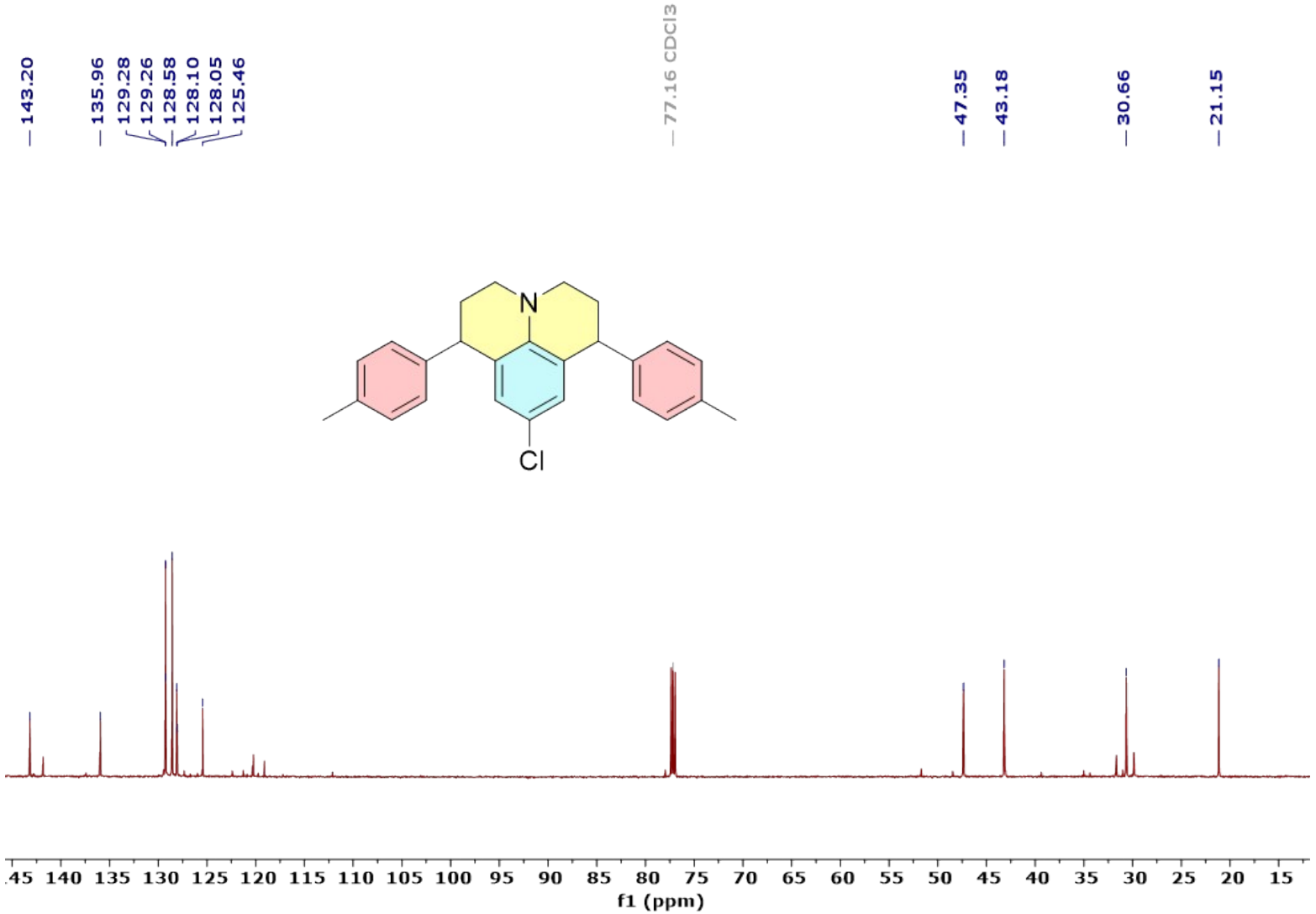


Fig. S71 ^{13}C NMR Spectrum of 9-chloro-1,7-di-p-tolyl-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline ($CDCl_3$, 151MHz, 298K)

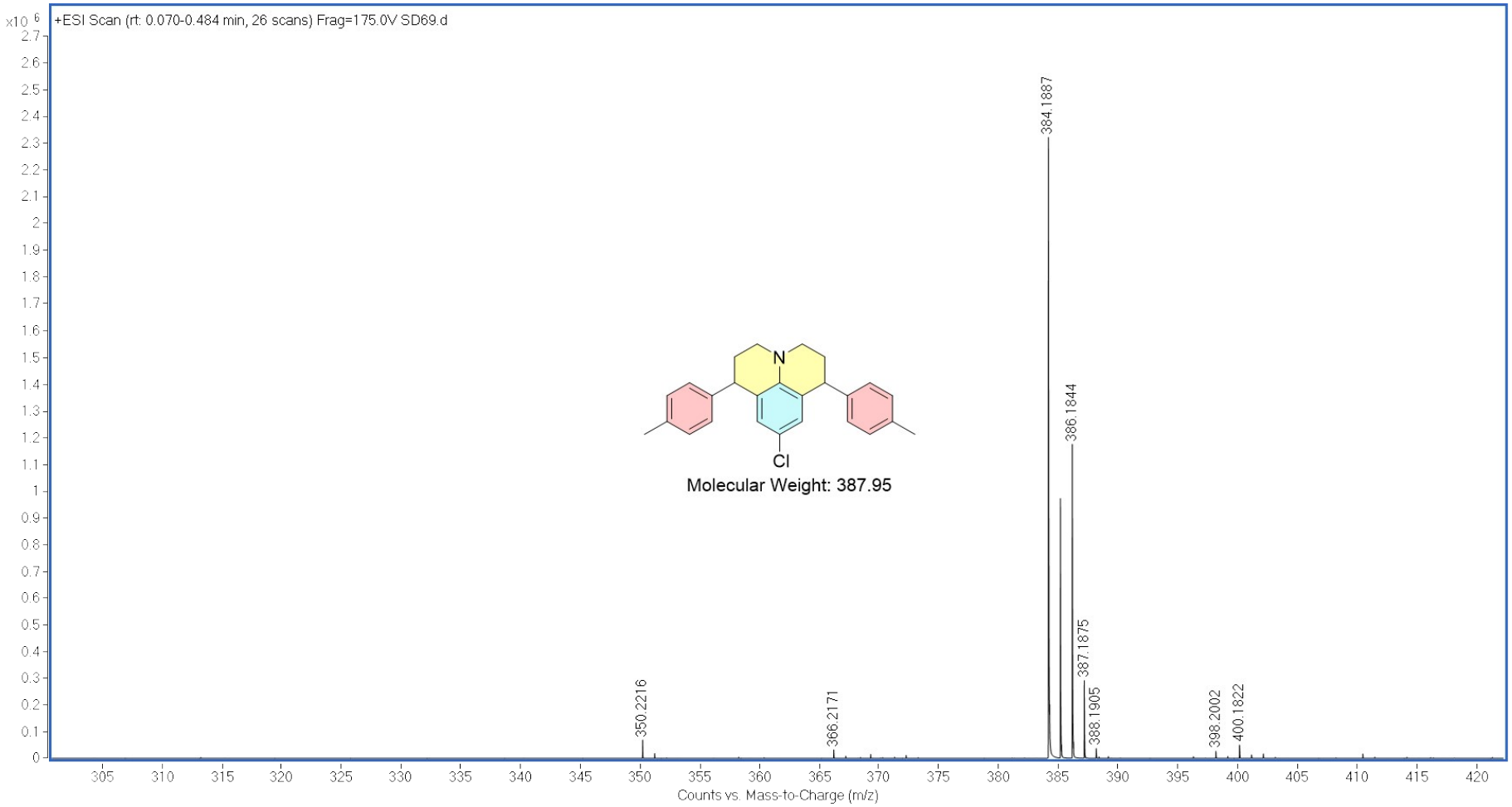


Fig. S72 ESI-MS Spectrum of 9-chloro-1,7-di-p-tolyl-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline

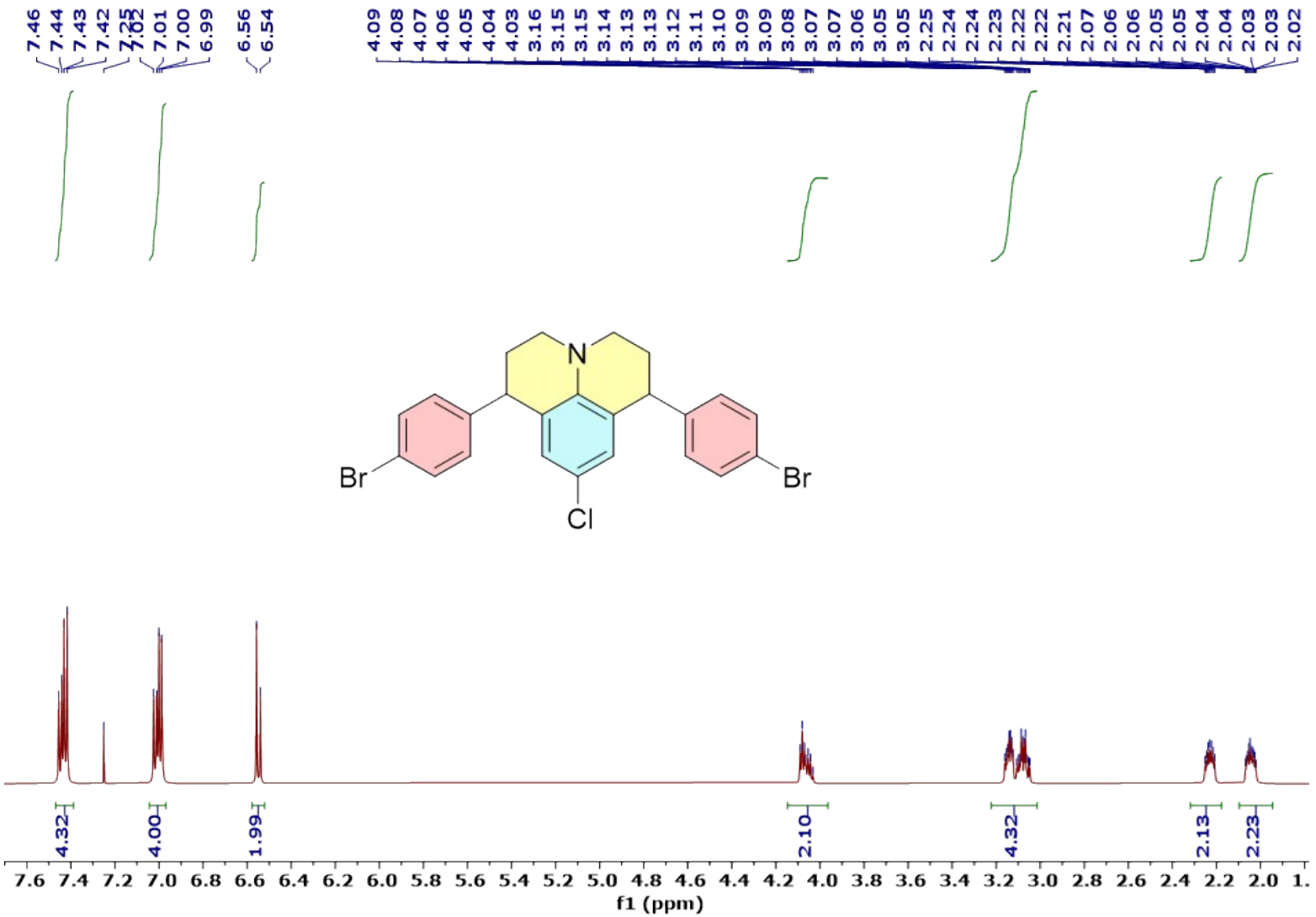


Fig. S73 ^{1}H NMR Spectrum of 1,7-bis(4-bromophenyl)-9-chloro-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline ($CDCl_3$, 600 MHz, 298K)

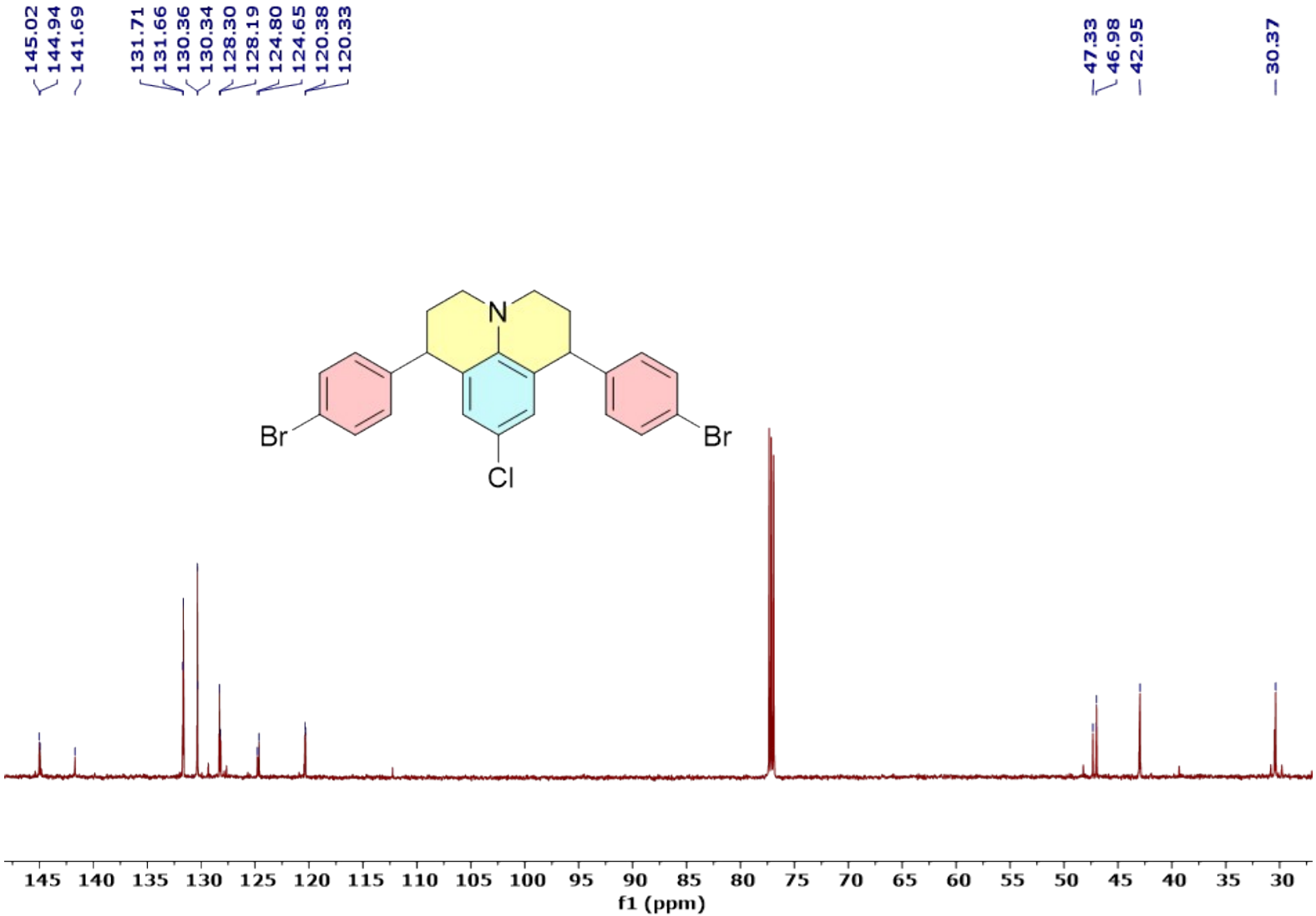


Fig. S74 ^{13}C NMR Spectrum of 1,7-bis(4-bromophenyl)-9-chloro-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline ($CDCl_3$, 151MHz, 298K)

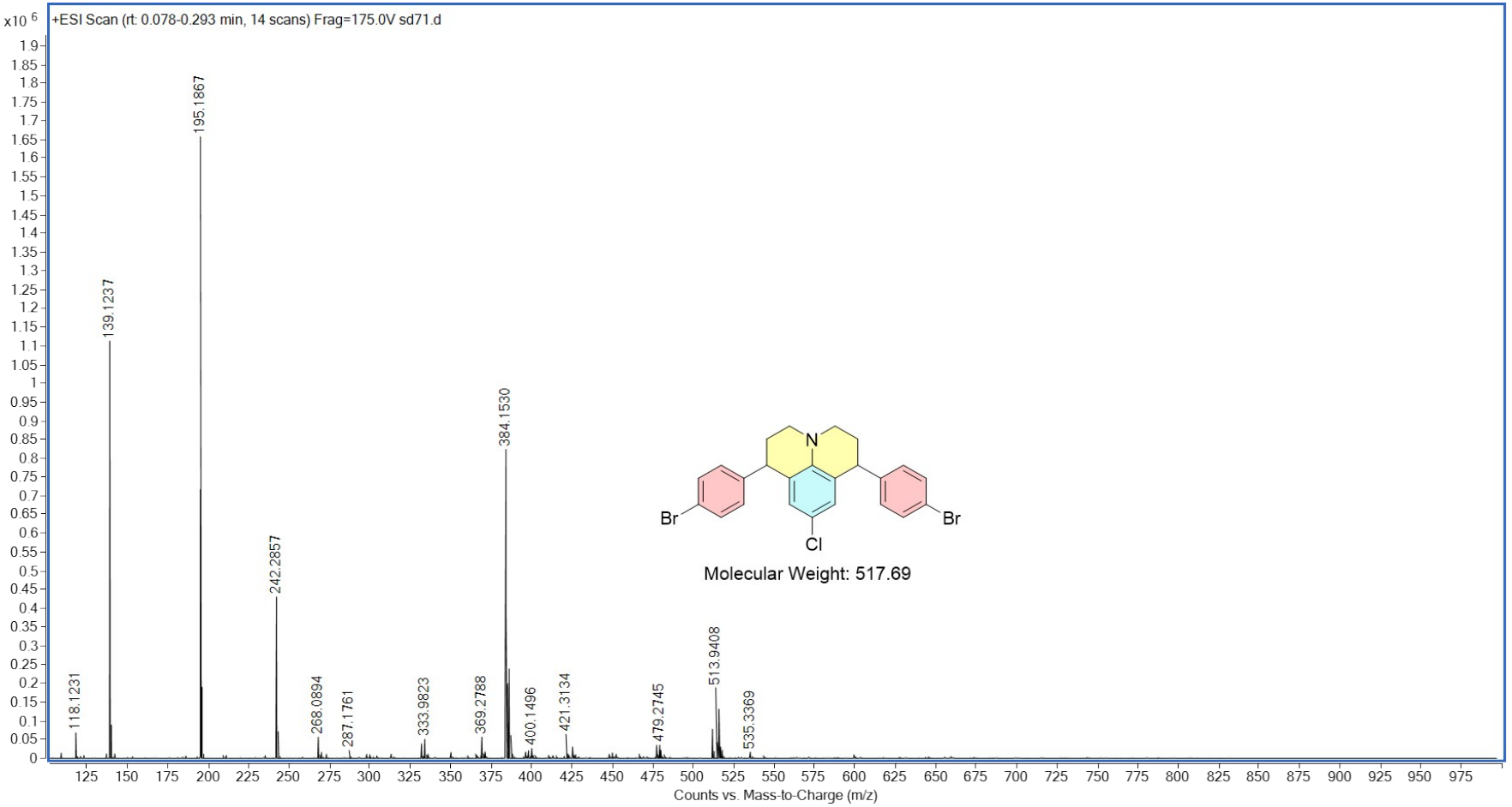


Fig. S75 ESI-MS Spectrum of 1,7-bis(4-bromophenyl)-9-chloro-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline

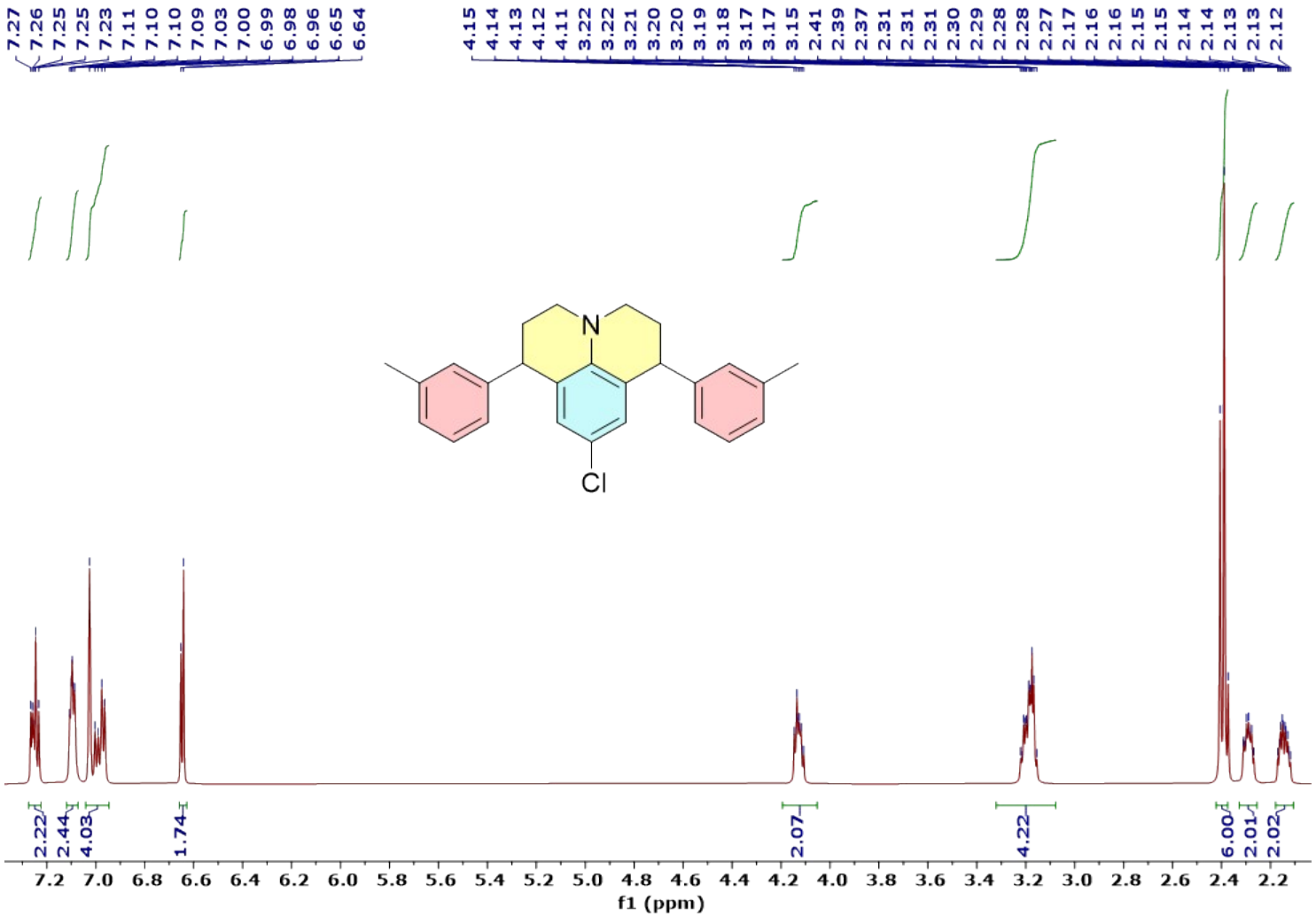


Fig. S76 ^{1}H NMR Spectrum of 1,7-bis(4-bromophenyl)-9-chloro-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline ($CDCl_3$, 600 MHz, 298K)

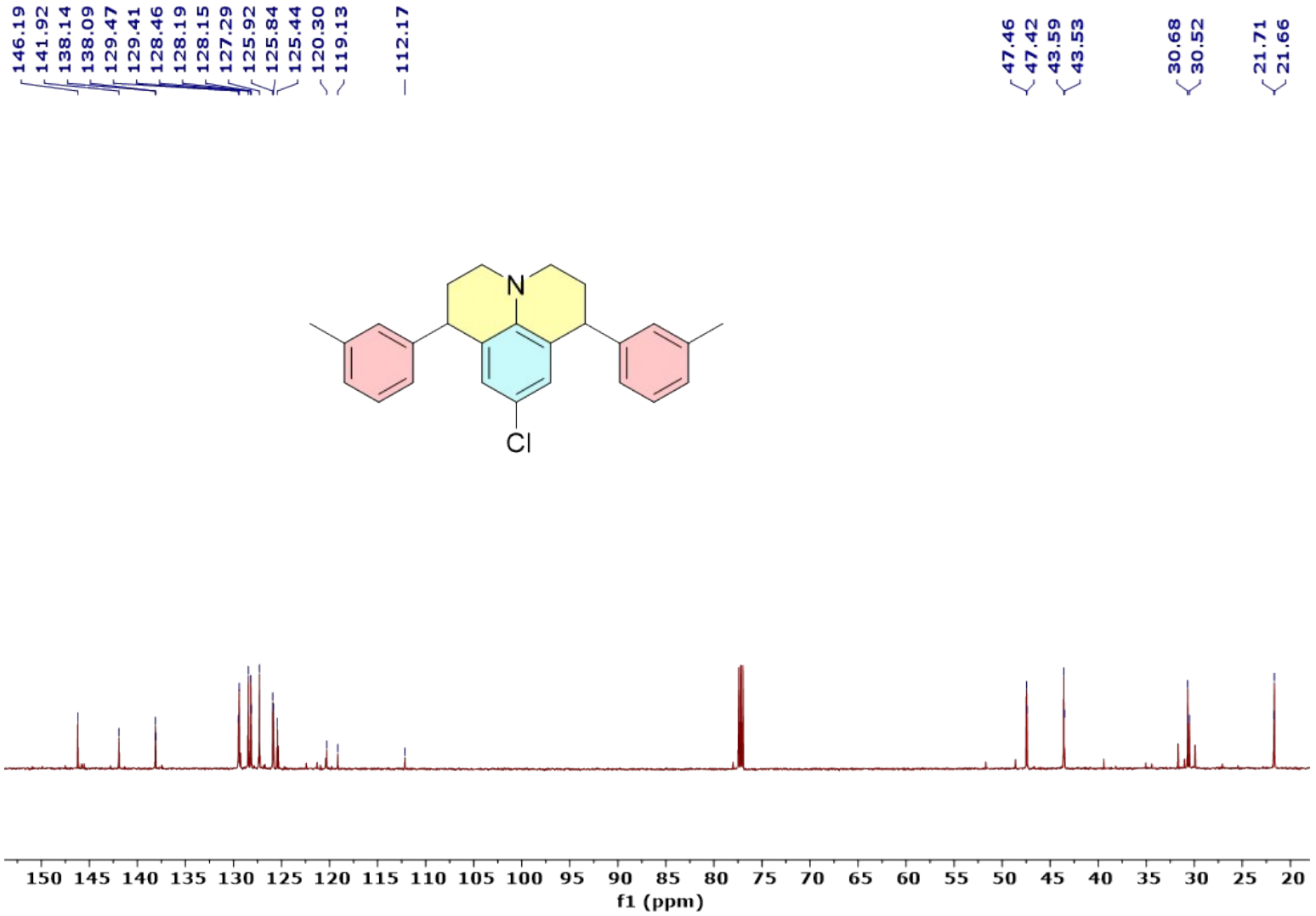


Fig. S77 ^{13}C NMR Spectrum of 1,7-bis(4-bromophenyl)-9-chloro-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline ($CDCl_3$, 151MHz, 298K)

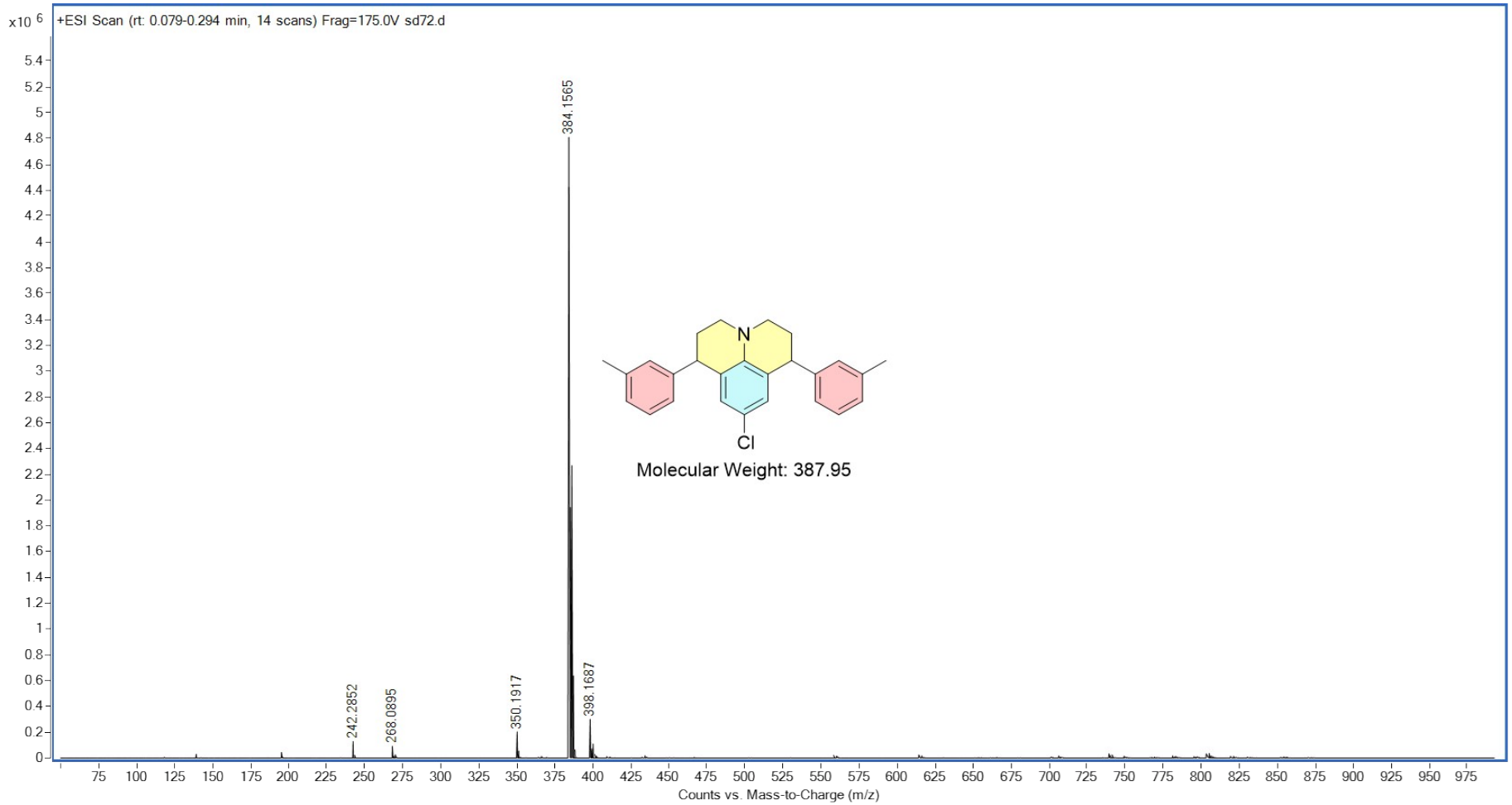


Fig. S78 ESI-MS Spectrum of 1,7-bis(4-bromophenyl)-9-chloro-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline

13. ^{1}H and ^{13}C NMR of quinoline intermediate

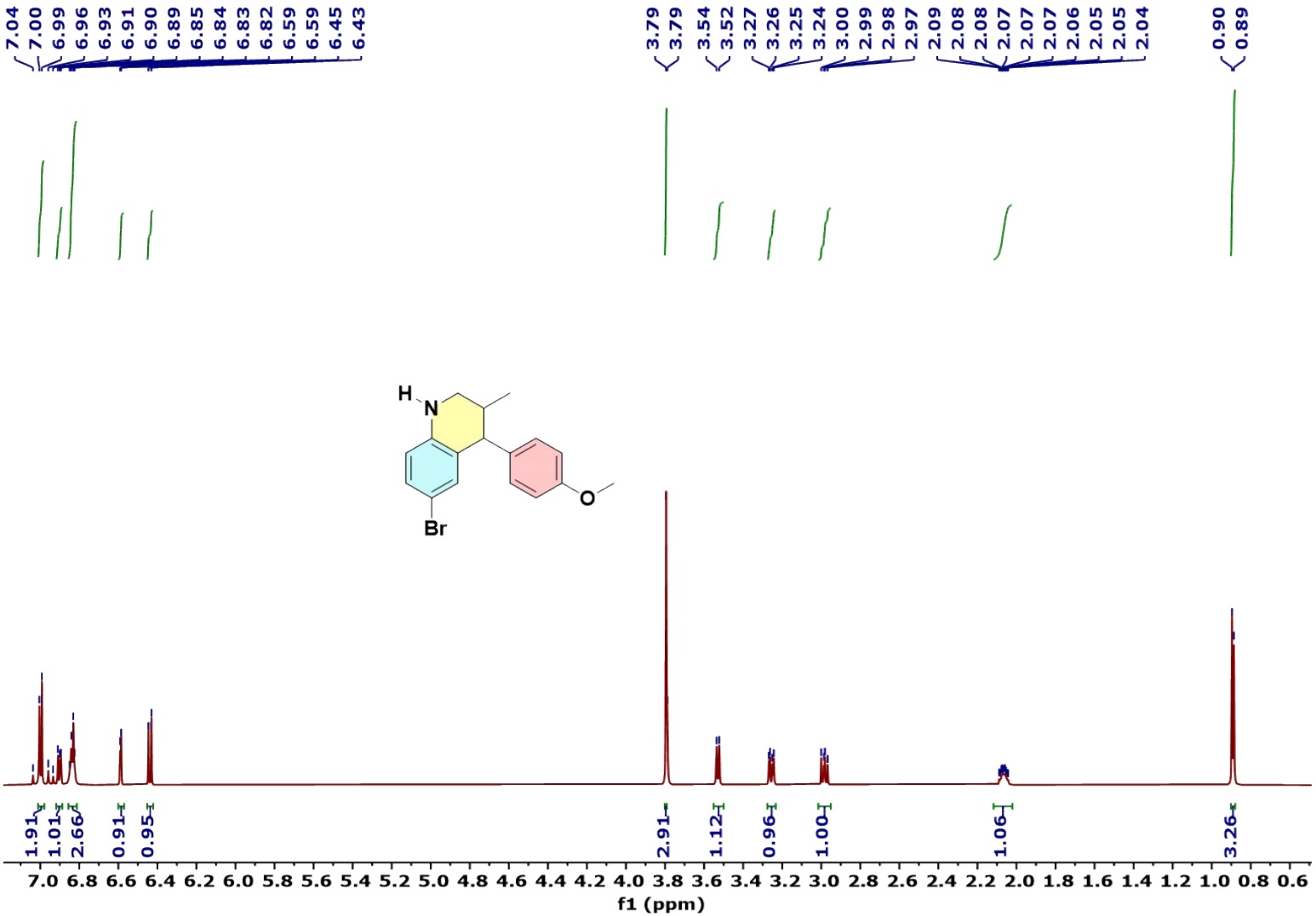


Fig. S79 ^{1}H NMR Spectrum of 6-bromo-4-(4-methoxyphenyl)-3-methyl-1,2,3,4-tetrahydroquinoline ($CDCl_3$, 600 MHz, 298K)

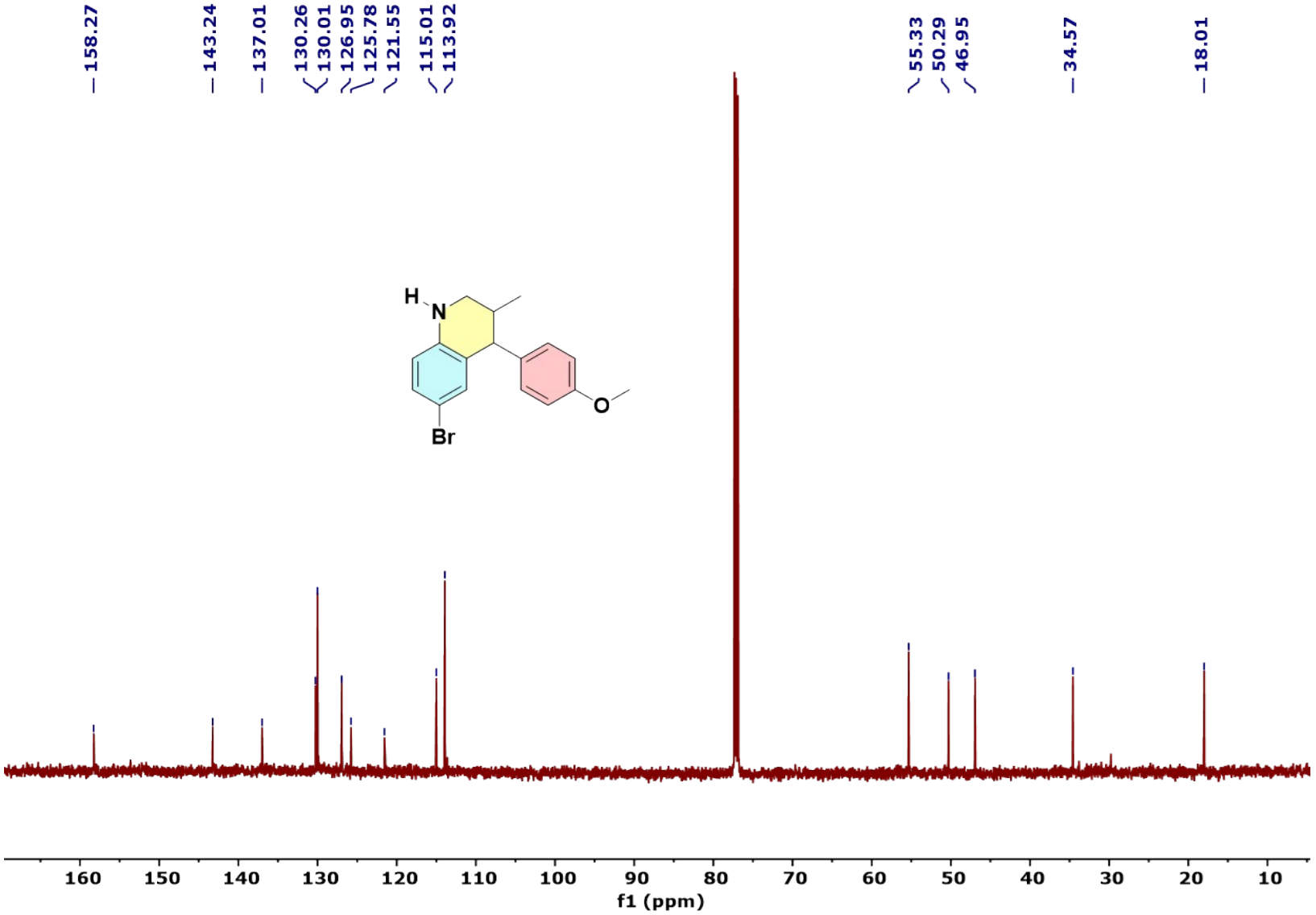


Fig. S80 ^{13}C NMR Spectrum of 6-bromo-4-(4-methoxyphenyl)-3-methyl-1,2,3,4-tetrahydroquinoline ($CDCl_3$, 151MHz, 298K)

14. ^{1}H and ^{13}C NMR of compound synthesised for kinetic study

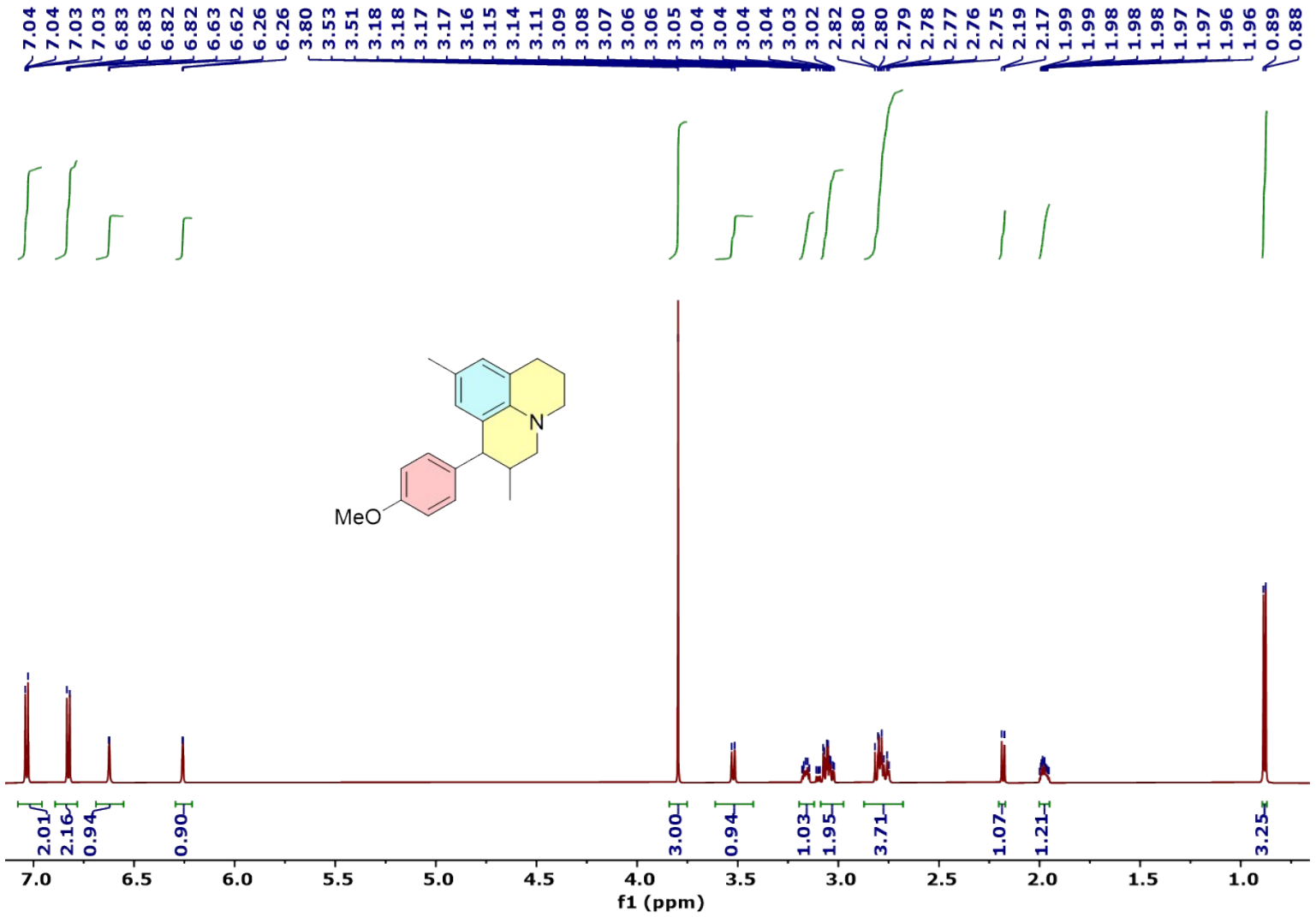


Fig. S81 ^{1}H NMR Spectrum of 1-(4-methoxyphenyl)-2,9-dimethyl-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline ($CDCl_3$, 600 MHz, 298K)

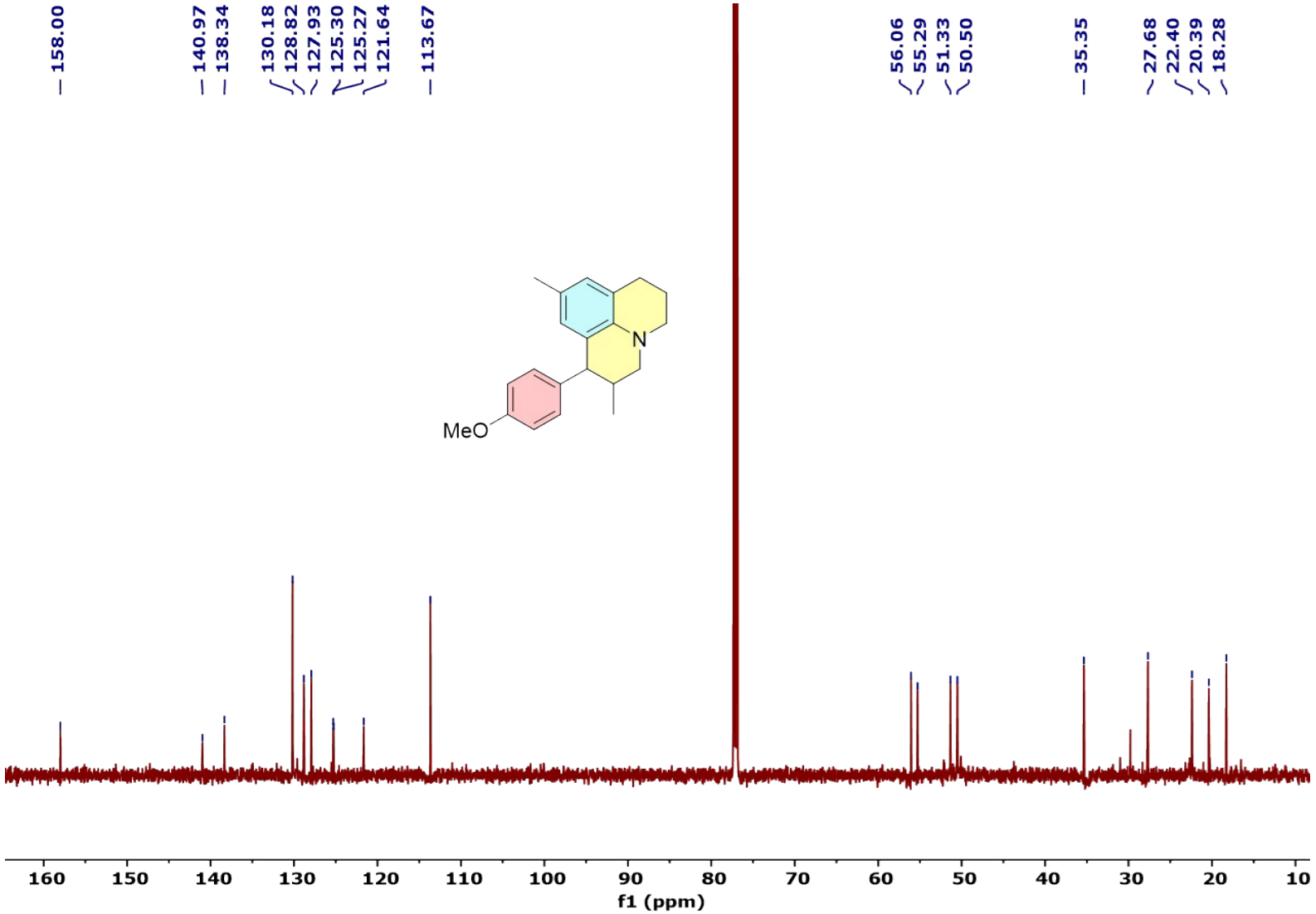


Fig. S82 ^{13}C NMR Spectrum of 1-(4-methoxyphenyl)-2,9-dimethyl-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline ($CDCl_3$, 151MHz, 298K)

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