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Supplementary Information for:

Radical Cascade Cyclization of 1,6-Enyne to Access Tricyclic Compounds by Cu/TBHP System

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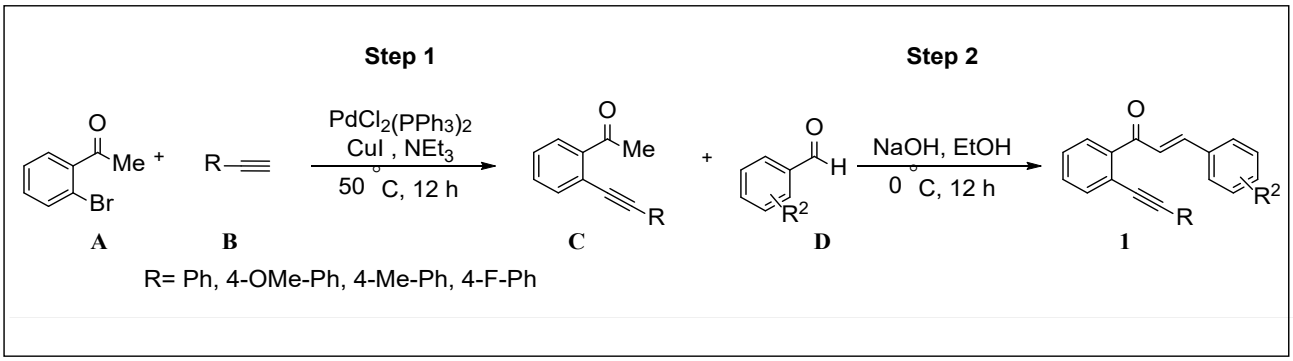
1. Experimental section

1.1. General information

All chemicals and solvents used in this study were purchased from chemical suppliers (Merck, Sigma-Aldrich, Fluka, and Alpha-Aesar) and used without further purification. The reaction process was monitored by TLC (thin-layer chromatography) using aluminum-coated plates of silica gel (MERCK, 60F254), via detection under UV fluorescence (wavelength of 254 nm). Chromatographic separations of products were carried out by flash column chromatography on MACHEREY-NAGEL silica gel 60 (230−400 mesh). Melting points (mp) were determined with an Electrothermal 9100 digital melting point apparatus and are uncorrected. Nuclear magnetic resonance (NMR) spectra (^{1}H and ^{13}C NMR) were recorded on a Bruker AVANCE 300, 400 and 500 MHz (DRX) spectrometer. Chemical shifts (δ) are quoted in ppm and the coupling constants (J) in Hz. Multiplets were indicated by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet, complex pattern), dd (doublet of doublet), ddd (doublet of doublet of doublet), td (triplet of doublet), and bs (broad singlet). The high-resolution mass spectrum (HRMS) (ESITOF) was recorded by using a Waters LCT Premier XE mass spectrometer.

1.2. General Experimental Procedures.

1.2.1. General procedure for preparation of (*E*)-3-aryl-1-(2-(arylethynyl)aryl)prop-2-en-1-one:[1]

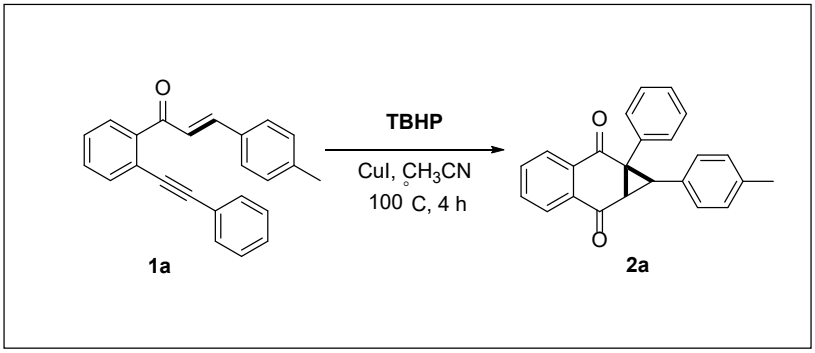


Step 1: 2'-Bromoacetophenone **A** (20 mmol), and acetylene **B** (24 mmol) were added to a mixture of CuI (0.2 mmol) and $PdCl_2(PPh_3)_2$ (0.4 mmol) in Et_3N (50 mL). The resulting mixture was heated under an argon atmosphere in an oil bath at 50 °C for 12 hours. After the reaction was completed,

the mixture was quenched by adding distilled water and extracted with DCM (three times). The combined organic layers were washed with brine, dried over Na_2SO_4, filtrated, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel, eluting with n-hexane and ethyl acetate (50:1) to afford the desired product **C**.

Step 2: To a stirred solution of benzaldehyde **D** (3.0 mmol) and 1-(2-(alkyl/arylethynyl)phenyl)ethan-1-one **C** (3.0 mmol) in 10 mL of ethanol at 0 °C was gradually added NaOH (4.5 mmol) in water (5 mL). Then, the resulting mixture was allowed to warm to room temperature and stirred for 12 h. Next, the solid product was filtered and washed repeatedly with cold water. Finally, recrystallization by ethanol afforded the desired products **1a-r**.

1. 2. 2. General Procedure for the Preparation of 1,1a-aryl-1a,7a-dihydro-1*H*-cyclopropa[*b*] naphthalene-2,7-dione (2a-t), Exemplified with 2a.



A mixture of (*E*)-1-(2 (phenylethynyl)phenyl)-3-(*p*-tolyl)prop-2-en-1-one **1a** (0.1 mmol, 0.032 g), TBHP (4.0 equiv., 0.4 mmol) and CuI (0.02 mmol, 0.004 g) in acetonitrile (1 mL) was heated at 100 °C in an oil bath for 4 h. The completion of the reaction was indicated by TLC monitoring, and the reaction mixture was cooled to room temperature. Then, distilled H_2O (5 mL) was added, and the reaction mixture was extracted with ethyl acetate (3 × 6 mL). The combined organic phase was dried over Na_2SO_4. The solvent was removed under the reduced pressure. The residue was purified by column chromatography using *n*-hexane-EtOAc (15:1) to afford the desired product **2a** (Yield 74%).

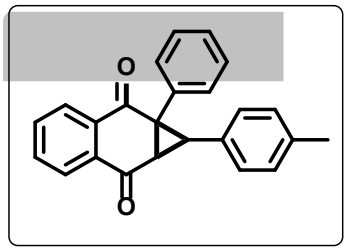
1. 2. 3. General Procedure for the Preparation of Compound 2a on a Scale of 1.0 mmol. The solution of (*E*)-1-(2-(phenylethynyl)phenyl)-3-(*p*-tolyl)prop-2-en-1-one (1.0 mmol, 0.322 g), TBHP (4.0 equiv., 4.0 mmol) and CuI (0.2 mmol, 0.040 g) in acetonitrile (5 mL) was heated at

100 °C in an oil bath for 4 h. After completion of the reaction as was indicated by TLC monitoring, the reaction mixture was cooled to ambient temperature. Then, distilled H_2O (10 mL) was added, and the reaction mixture was extracted with ethyl acetate (3 × 6 mL). The combined organic phase was dried over Na_2SO_4. The solvent was removed under reduced pressure. The residue was purified by column chromatography using *n*-hexane/EtOAc (15:1) as eluent to afford the desired pure product **2a** in 45% (152 mg) yield.

The Postreaction Based on the Reaction of Compound 2g with Hydroxylamine Hydrochloride.[2]

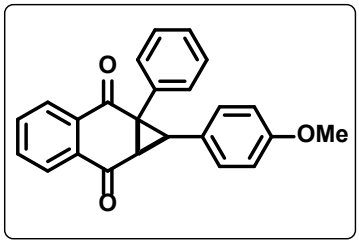
A typical postmodification reaction based on the reaction of compound **2g** with hydroxylamine hydrochloride was carried out as follows: a mixture of the product **2g** (0.5 mmol, 0.176 g), pyridine (1.4 mmol, 0.111 g), and hydroxylamine hydrochloride (0.75 mmol, 0.052 g) in ethanol (2 mL) was heated at 60 °C in an oil bath for 75 min and then cooled to 22 °C. Then, distilled H_2O (2 mL) was added, and the reaction mixture was extracted with ethyl acetate (2 × 2 mL). The organic extract was combined, washed successively with 1 M HCl (1.2 mL), and dried over anhydrous $NaSO_4$ (0.50 g) for 15 min. The extract was gravity filtered through filter paper and concentrated in a rotary evaporator. Finally, recrystallization by ethanol afforded the desired product **3g**.

1a-Phenyl-1-(*p*-tolyl)-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (2a).



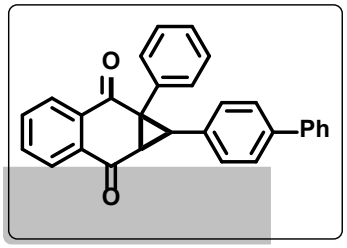
White solid (25 mg, yield 74%), mp 182-185 °C, [lit[1a] mp 180-182 °C]. ^{1}H NMR (300 MHz, $CDCl_3$) δ_H = 8.25 – 8.11 (m, 2H), 7.88 – 7.80 (m, 2H), 7.33 – 7.25 (m, 3H), 7.22 – 7.13 (m, 2H), 6.93 (d, J = 8.1 Hz, 2H), 6.67 (d, J = 8.1 Hz, 2H), 3.67 (d, J = 5.7 Hz, 1H), 3.43 (d, J = 5.7 Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C = 192.9, 191.2, 137.4, 134.5, 134.3, 134.2, 134.1, 132.6, 131.9, 131.8, 130.3, 128.8, 128.1, 128.0, 127.9, 126.8, 51.0, 43.1, 40.2, 21.1; HRMS-ESI (ESI-TOF) m/z: calc. for $C_{24}H_{19}O_2$ $[M+H]^+$ 339.1379, found 339.1376.

1-(4-Methoxyphenyl)-1a-phenyl-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione



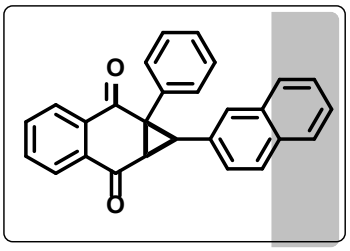
(**2b**). Yellow solid (28 mg, yield 79%), mp 205-508 °C, [lit[1a] mp 191-193 °C]. ^{1}H NMR (300 MHz, $CDCl_3$) δ_H = 8.23 – 8.05 (m, 2H), 7.84 – 7.75 (m, 2H), 7.26 – 7.21 (m, 3H), 7.18 -7.09 (m, 2H), 6.67 (d, *J* = 9.0 Hz, 2H), 6.62 (d, *J* = 9.0 Hz, 2H), 3.71 (s, 3H), 3.60 (d, *J* = 5.7 Hz, 1H), 3.38 (d, *J* = 5.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C = 192.8, 191.1, 159.0, 134.4, 134.1, 132.6, 132.6, 131.9, 131.9, 129.1, 128.1, 128.1, 128.0, 126.8, 125.4, 113.5, 55.1, 50.9, 42.9, 40.3; HRMS (ESI-TOF) m/z: calc. for $C_{24}H_{19}O_3$ $[M+H]^+$ 355.1328, found 355.1334.

1-([1,1'-Biphenyl]-4-yl)-1a-phenyl-1a,7a-dihydro-1*H*-1cyclopropa[*b*]naphthalene-2,7-dione



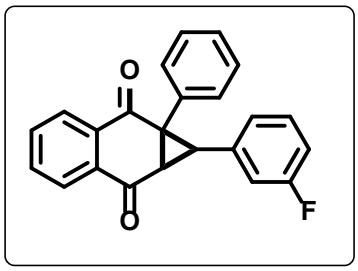
(2c). White solid (32 mg, yield 80%), mp 189-192 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ_H = 8.26 – 8.07 (m, 2H), 7.85 – 7.77 (m, 2H), 7.50 (d, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.1 Hz, 2H), 7.37 – 7.31 (m, 3H), 7.30 – 7.23 (m, 3H), 7.22 – 7.16 (m, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 3.70 (d, *J* = 5.7 Hz, 1H), 3.47 (d, *J* = 5.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C = 192.6, 190.9, 140.3, 140.1, 134.5, 134.2, 132.5, 132.5, 131.9, 131.7, 128.7, 128.5, 128.2, 128.1, 128.1, 128.1, 127.4, 126.9, 126.8, 126.6, 51.0, 42.9, 40.3; HRMS (ESI-TOF) m/z: calc. for $C_{29}H_{21}O_2$ $[M+H]^+$ 401.1535, found 401.1529.

1-(Naphthalen-2-yl)-1a-phenyl-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (**2d**).



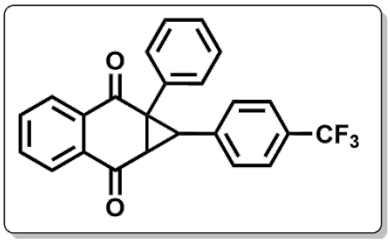
White solid (28 mg, yield 75%), mp 193-196 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ_H = 8.26 – 8.08 (m, 2H), 7.86 – 7.80 (m, 2H), 7.74 – 7.70 (m, 1H), 7.65 – 7.59 (m, 1H), 7.55 (d, *J* = 8.7 Hz, 1H), 7.45 – 7.40 (m, 3H), 7.24 – 7.15 (m, 5H), 6.74 (d, *J* = 8.7 Hz, 1H), 3.83 (d, *J* = 5.7 Hz, 1H), 3.62 (d, *J* = 5.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C = 192.1, 190.5, 134.0, 133.7, 132.4, 132.2, 132.1, 131.4, 131.2, 130.6, 127.8, 127.7, 127.6, 127.3, 127.2, 127.1, 126.4, 125.9, 125.8, 125.7, 124.9, 124.8, 50.5, 42.8, 39.7; HRMS (ESI-TOF) m/z: calc. for $C_{27}H_{19}O_2$ $[M+H]^+$ 375.1379, found 375.1375.

1-(3-Fluorophenyl)-1a-phenyl-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (2e).



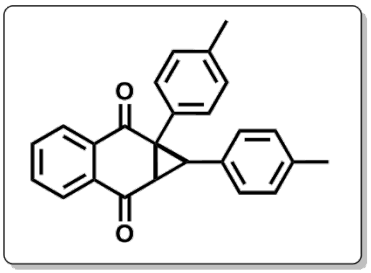
White solid (26 mg, yield 76%), mp 180 – 183 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ_H = 8.20 – 8.08 (m, 2H), 7.85 – 7.72 (m, 2H), 7.31 – 7.20 (m, 3H), 7.19 – 7.10 (m, 2H), 7.08 – 7.00 (m, 1H), 6.81 (t, *J* = 8.3 Hz, 1H), 6.56 (d, *J* = 7.9 Hz, 1H), 6.49 – 6.39 (m, 1H), 3.62 (d, *J* = 5.6 Hz, 1H), 3.39 (d, *J* = 5.6 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ_C = 192.3, 190.7, 162.4 (d, $^{1}J_{C-F}$= 245 Hz), 136.0 (d, $^{3}J_{C-F}$=7.9 Hz), 134.6, 134.3, 132.4, 132.4, 131.7, 131.3, 129. (d, $^{3}J_{C-F}$=8.4 Hz), 128.3, 128.2, 128.2, 126.9, 123.8 (d, $^{4}J_{C-F}$= 2.7 Hz), 115.0 (d, $^{2}J_{C-F}$= 22.8 Hz), 114.6 (d, $^{2}J_{C-F}$= 20.8 Hz), 50.7, 42.2, 39.8.; ^{19}F NMR (282 MHz, $CDCl_3$) δ_F = -112.9 (s, 1F); HRMS (ESI-TOF) m/z: calc. for $C_{23}H_{16}FO_2$ $[M+H]^+$ 343.1128, found 343.1136.

1a-Phenyl-1-(4-(trifluoromethyl)phenyl)-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (2f).

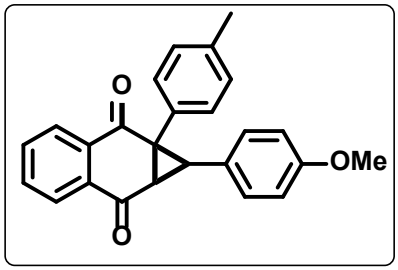


White solid (22 mg, yield 56%), mp 178 - 181 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 8.23 – 8.20 (m, 1H), 8.18 – 8.14 (m, 1H), 7.88 – 7.84 (m, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.33 – 7.30 (m, 3H), 7.20 – 7.16 (m, 2H), 6.90 (d, *J* = 8.3 Hz, 2H), 3.72 (d, *J* = 5.6 Hz, 1H), 3.49 (d, *J* = 5.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C = 192.2, 190.6, 137.7, 134.7, 134.5, 132.3 (q, $^{3}J_{C-F}$ =3.3 Hz), 131.8, 131.2, 131.1, 129.7 (q, $^{2}J_{C-F}$ = 33.3 Hz), 128.4, 128.3, 128.2 (2C), 127.0, 125.1, 123.9 (q, $^{1}J_{C-F}$ = 270.9 Hz), 50.8, 42.0, 40.0. ^{19}F NMR (377 MHz, $CDCl_3$) δ_F = -62.6 (s, 3F); HRMS (ESI-TOF) m/z: calc. for $C_{24}H_{16}F_3O_2$ $[M+H]^+$ 393.1096, found 393.1098.

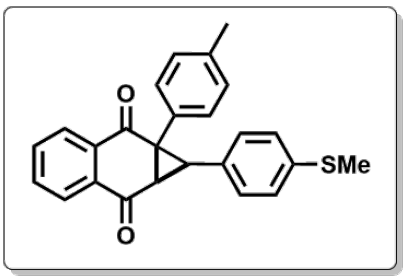
1,1a-Di-*p*-tolyl-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione(2g). White solid (25 mg, yield 71%), mp 217-220 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 8.20 – 8.16 (m, 1H), 8.14 – 8.10 (m, 1H), 7.82 – 7.77 (m, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 7.7 Hz, 2H), 6.67 (d, *J* = 8.4 Hz, 2H), 3.62 (d, *J* = 5.7 Hz, 1H), 3.39 (d, *J* = 5.7 Hz, 1H), 2.32 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C = 192.9, 191.4, 137.7, 137.2, 134.4, 134.1, 132.6, 132.6, 131.7, 130.5, 128.9, 128.8, 128.7, 128.1, 128.0, 126.7, 50.7, 43.1, 40.4, 21.2, 21.0; HRMS (ESI-TOF) m/z: calc. for $C_{25}H_{21}O_2$ $[M+H]^+$ 353.1536, found 353.1544.



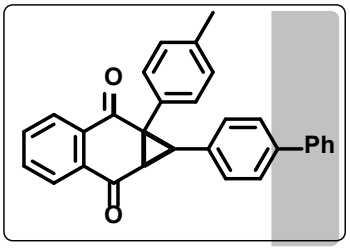
1-(4-Methoxyphenyl)-1a-(*p*-tolyl)-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (2h). White solid (31 mg, yield 84%), mp 130-133 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 8.19 – 8.14 (m, 1H), 8.12 – 8.08 (m, 1H), 7.81 – 7.76 (m, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 7.04 (d, *J* = 8.2 Hz, 2H), 6.70 (d, *J* = 9.0 Hz, 2H), 6.64 (d, *J* = 8.8 Hz, 2H), 3.71 (s, 3H), 3.57 (d, *J* = 5.7 Hz, 1H), 3.37 (d, *J* = 5.7 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C = 192.9, 191.4, 159.0, 137.7, 134.4, 134.1, 132.7, 132.6, 131.7, 129.2, 128.9, 128.8, 128.1, 126.7, 125.6, 113.6, 55.2, 50.7, 42.8, 40.5, 21.2; HRMS (ESI-TOF) m/z: calc. for $C_{25}H_{21}O_3$ $[M+H]^+$ 369.1484, found 369.1485.



1-(4-(Methylthio)phenyl)-1a-(*p*-tolyl)-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (**2i**). Yellow solid (28 mg, yield 73%), mp 206-209 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 8.20 – 8.15 (m, 1H), 8.13 – 8.09 (m, 1H), 7.83 – 7.77 (m, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 7.03 (d, *J* = 8.3 Hz, 2H), 6.97 (d, *J* = 8.6 Hz, 2H), 6.67 (d, *J* = 8.4 Hz, 2H), 3.58 (d, *J* = 5.6 Hz, 1H), 3.36 (d, *J* = 5.6 Hz, 1H), 2.41 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C = 192.7, 191.2, 138.0, 137.9, 134.4, 134.1, 132.5, 131.6, 130.3, 129.1, 129.0, 128.5, 128.1, 126.8, 125.9, 123.3, 50.7, 42.8, 40.4, 21.2, 15.5; HRMS (ESI-TOF) m/z: calc. for $C_{25}H_{21}O_2S$ $[M+H]^+$ 385.1256, found 385.1261.

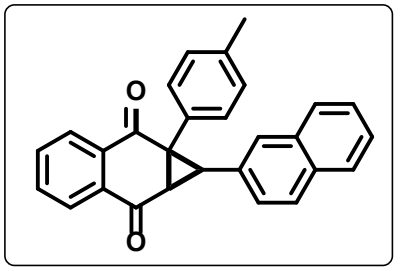


1-([1,1'-Biphenyl]-4-yl)-1a-(*p*-tolyl)-1a,7a-dihydro-1*H*-cyclopropa[*b*] naphthalene-2,7-dione



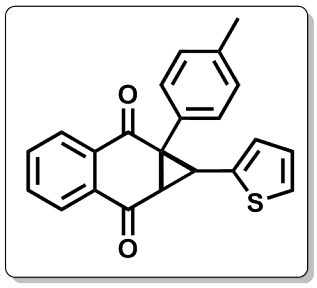
(2j). White solid (34 mg, yield 82%), mp 122-125 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 8.21 – 8.18 (m, 1H), 8.15-8.12 (m, 1H), 7.84 – 7.78 (m, 2H), 7.54 – 7.49 (m, 2H), 7.42 – 7.38 (m, 2H), 7.36 (d, *J* = 8.6 Hz, 2H), 7.34 – 7.31 (m, 1H), 7.09 – 7.05 (m, 4H), 6.83 (d, *J* = 8.3 Hz, 2H), 3.67 (d, *J* = 5.6 Hz, 1H), 3.45 (d, *J* = 5.7 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C = 192.8, 191.3, 140.2, 137.9, 137.4, 136.4, 135.7, 134.5, 134.2, 132.7, 132.6, 131.7, 129.0, 128.8, 128.5, 128.2, 127.5, 126.9, 126.8, 126.7, 50.8, 43.0, 40.5, 21.3; HRMS (ESI-TOF) m/z: calc. for $C_{30}H_{23}O_2$ $[M+H]^+$ 415.1692, found 415.1686.

1-(Naphthalen-2-yl)-1a-(*p*-tolyl)-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione



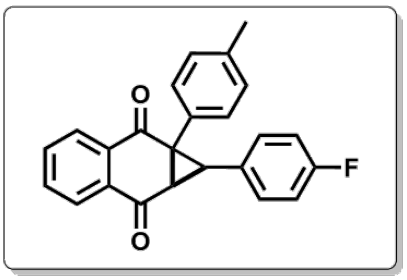
(2k). White solid (28 mg, yield 72%), mp 200-203 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 8.24 – 8.18 (m, 1H), 8.15 – 8.13 (m, 1H), 7.86 – 7.79 (m, 2H), 7.73 – 7.69 (m, 1H), 7.63 – 7.58 (m, 1H), 7.56 (d, *J* = 8.7 Hz, 1H), 7.45 – 7.36 (m, 3H), 7.07 (d, *J* = 8.3 Hz, 2H), 7.02 (d, *J* = 7.9 Hz, 2H), 6.76 (dd, *J* = 8.6, 2.0 Hz, 1H), 3.79 (d, *J* = 5.6 Hz, 1H), 3.59 (d, *J* = 5.7 Hz, 1H)), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C = 193.0, 191.4, 137.9, 137.2, 134.5, 134.3, 132.9, 132.6, 132.5, 131.6, 131.2, 130.9, 129.0, 128.5, 128.2, 127.9, 127.7, 127.6, 126.8, 126.3, 126.2, 125.3, 50.8, 43.5, 40.4, 21.2; HRMS (ESI-TOF) m/z: calc. for $C_{28}H_{21}O_2$ $[M+H]^+$ 389.1535, found 389.1537.

1-(Thiophen-2-yl)-1a-(*p*-tolyl)-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione(2l).



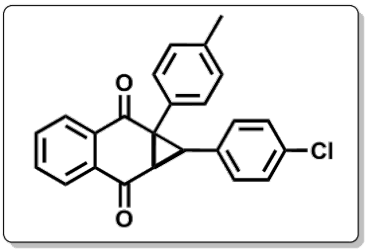
Yellow solid (23 mg, yield 67%), mp 199-202 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 8.19 – 8.14 (m, 1H), 8.13 - 8.08 (m, 1H), 7.82 – 7.78 (m, 2H),7.15 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 7.05 (dd, *J* = 5.6, 1.2 Hz, 1H), 6.76 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.53 – 6.50 (m, 1H), 3.60 (d, *J* = 5.5 Hz, 1H), 3.54 (d, *J* = 5.5 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C = 192.1, 190.8, 138.2, 137.2, 134.6, 134.3, 132.5, 132.4, 131.6, 128.9, 128.6, 128.2, 126.9, 126.8, 126.6, 125.3, 50.8, 42.3, 38.6, 21.3; HRMS (ESI-TOF) m/z: calc. for $C_{22}H_{17}O_2S$ $[M+H]^+$ 345.0943, found 345.0937.

1-(4-Fluorophenyl)-1a-(*p*-tolyl)-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione



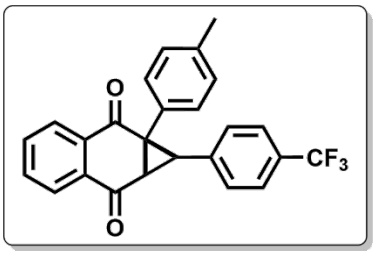
(2m). White solid (26 mg, yield 73%), mp 185-188 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 8.21 – 8.19 (m, 1H), 8.16 – 8.13 (m, 1H), 7.87 – 7.80 (m, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 7.05 (d, *J* = 8.2 Hz, 2H), 6.84 (t, *J* = 8.7 Hz, 2H), 6.80 – 6.74 (m, 2H), 3.61 (d, *J* = 5.6 Hz, 1H), 3.42 (d, *J* = 5.6 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C = 192.7, 191.2, 162.1 (d, $^{1}J_{C\text{-}F}$ = 243.8 Hz), 138.0, 134.6, 134.3, 132.5, 131.7, 129.7, 129.6, 129.4, 129.0, 128.3, 128.2, 126.8, 115.2 (d, $^{2}J_{C\text{-}F}$ = 21.6 Hz), 50.5, 42.3, 40.2, 21.3; HRMS (ESI-TOF) m/z: calc. for $C_{24}H_{18}FO_2$, $[M+H]^+$ 357.1285, found 357.1279.

1-(4-Chlorophenyl)-1a-(*p*-tolyl)-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione(2n).

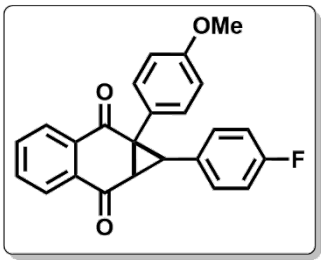


White solid (26 mg, yield 70%), mp 198-201 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 8.20 – 8.15 (m, 1H), 8.13 – 8.10 (m, 1H), 7.84 – 7.78 (m, 2H), 7.10 – 7.06 (m, 4H), 7.02 (d, *J* = 8.2 Hz, 2H), 6.70 (d, *J* = 8.6 Hz, 2H), 3.58 (d, *J* = 5.6 Hz, 1H), 3.36 (d, *J* = 5.6 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C = 192.5, 191.0, 138.0, 134.5, 134.4, 134.2, 133.4, 132.4, 132.2, 131.6, 129.3, 129.0, 128.3, 128.2, 128.1, 126.8, 50.5, 42.2, 40.2, 21.2.; HRMS (ESI-TOF) m/z: calc. for $C_{24}H_{18}ClO_2$, $[M+H]^+$ 373.0989, found 373.0992.

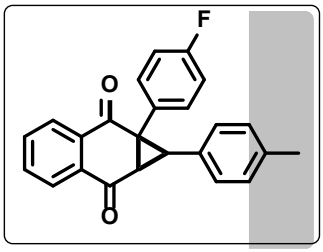
1a-(*p*-Tolyl)-1-(4-(trifluoromethyl)phenyl)-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7 dione (2o). White solid (25 mg, yield 62%), mp 176-179 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 8.21 – 8.15 (m, 1H), 8.14 – 8.09 (m, 1H), 7.85 – 7.79 (m, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 7.8 Hz, 2H), 7.02 (d, *J* = 8.3 Hz, 2H), 6.88 (d, *J* = 8.3 Hz, 2H), 3.65 (d, *J* = 5.6 Hz, 1H), 3.43 (d, *J* = 5.6 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C = 192.3, 190.9, 138.3, 137.8, 134.7, 134.4, 132.4, 131.9, 131.6, 130.9, 129.8 (q, $^{2}J_{C\text{-}F}$ = 32.5 Hz), 129.2, 128.4, 128.3, 126.9, 125.1, 123.9 (q, $^{1}J_{C\text{-}F}$ = 269.0 Hz), 50.6, 42.1, 40.2, 21.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ_F = -62.6 (s, 3F); HRMS (ESI-TOF) m/z: calc. for $C_{25}H_{18}F_3O_2$ $[M+H]^+$ 407.1253, found 407.1257.



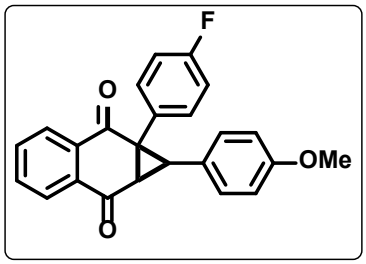
1-(4-Fluorophenyl)-1a-(4-methoxyphenyl)-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (**2p**). White solid (26 mg, yield 70%) mp 178-181 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 8.19 – 8.15 (m, 1H), 8.13-8.09 (m, 1H), 7.83 – 7.77 (m, 2H), 7.05 (d, *J* = 8.8 Hz, 1H), 7.04 – 7.02 (m, 1H), 6.84 – 6.79 (m, 3H), 6.79 – 6.77 (m, 1H), 6.77 – 6.72 (m, 2H), 3.78 (s, 3H), 3.57 (d, *J* = 5.6 Hz, 1H), 3.37 (d, *J* = 5.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C = 192.6, 191.3, 162.1 (d, $^{1}J_{C\text{-}F}$ = 245.4 Hz), 159.3, 134.4 (d, $^{2}J_{C\text{-}F}$ = 33.2 Hz), 132.9, 132.5, 129.7, 129.6, 129.3 (d, $^{3}J_{C\text{-}F}$ = 3.2 Hz), 128.1, 126.8, 123.4, 115.2, 115.1, 113.7, 55.2, 50.1, 42.3, 40.4.. ^{19}F NMR (470 MHz, $CDCl_3$) δ_F = -114.1 (s,1F); HRMS (ESI-TOF) m/z: calc. for $C_{24}H_{18}FO_3$ $[M+H]^+$ 373.1234, found 373.1236.



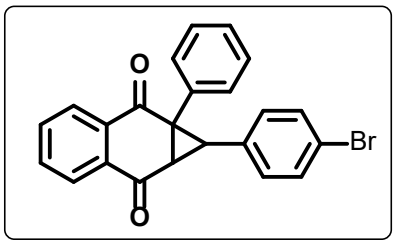
1a-(4-Fluorophenyl)-1-(*p*-tolyl)-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (**2q**). White solid (25 mg, yield 70%), mp 205-208 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ_H = 8.23 – 8.05 (m, 2H), 7.84 – 7.75 (m, 2H), 7.16 – 7.06 (m, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 8.1 Hz, 2H), 6.65 (d, *J* = 8.1 Hz, 2H), 3.61 (d, *J* = 5.8 Hz, 1H), 3.40 (d, *J* = 5.8 Hz, 1H), 2.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C = 192.0, 190.5, 161.7 (d, $^{1}J_{C\text{-}F}$ = 222.0 Hz), 137.1, 133.9, 133.8, 133.1, 133.0, 132.1, 132.0, 129.6, 128.5, 127.6, 127.4, 126.4, 114.6 (d, $^{2}J_{C\text{-}F}$ = 21.5 Hz), 49.6, 42.5, 39.5, 20.5; ^{19}F NMR (282 MHz, $CDCl_3$) δ_F = -113.6 (s,1F). HRMS (ESI-TOF) m/z: calc. for $C_{24}H_{18}FO_2$, $[M+H]^+$ 357.1285, found 357.1285.



1a-(4-Fluorophenyl)-1-(4-methoxyphenyl)-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (2r). White solid (28 mg, yield 75%), mp 167-170 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 8.19 – 8.13 (m, 1H), 8.12 – 8.08 (m, 1H), 7.83 – 7.76 (m, 2H), 7.12 (dd, *J* = 8.9, 5.2 Hz, 2H), 6.95 (t, *J* = 8.9 Hz, 2H), 6.68 (d, *J* = 9.3 Hz, 2H), 6.65 (d, *J* = 9.1 Hz, 2H), 3.72 (s, 3H), 3.58 (d, *J* = 5.7 Hz, 1H), 3.38 (d, *J* = 5.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C = 192.5, 191.1, 162.4 (d, $^{1}J_{C\text{-}F}$ = 242.5 Hz), 159.1, 134.5, 134.3, 133.6, 132.6, 132.4, 129.1, 128.1, 127.8, 126.9, 125.1, 115.2 (d, $^{2}J_{C\text{-}F}$ = 24.0 Hz), 113.6, 55.2, 50.1, 42.9, 40.2; ^{19}F NMR (282 MHz, $CDCl_3$) δ_F = -104.2 (s,1F); HRMS (ESI-TOF): calc. for $C_{24}H_{18}FO_3$ $[M+H]^+$ 373.1234, found 373.1228.

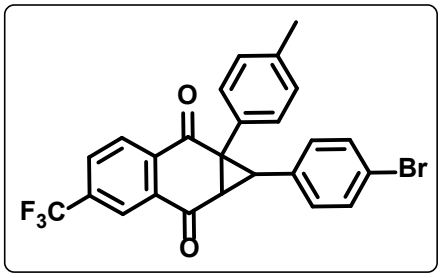


1-(4-Bromophenyl)-1a-phenyl-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (2s)



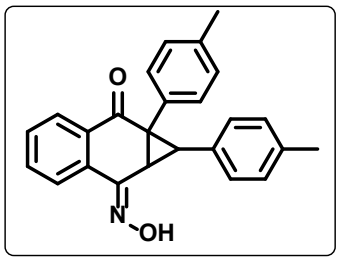
White solid (33 mg, yield 82%), mp 186-189 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 8.21 – 8.17 (m, 1H), 8.14 - 8.11 (m, 1H), 7.85 – 7.80 (m, 2H), 7.31 – 7.27 (m, 3H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.17 – 7.13 (m , 2H), 6.63 (d, *J* = 8.5 Hz, 2H), 3.62 (d, *J* = 5.7 Hz, 1H), 3.38 (d, *J* = 5.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C = 192.3, 190.7, 134.6, 134.3, 132.6, 132.4, 132.4, 131.8, 131.3, 131.2, 129.6, 128.3, 128.1, 126.9, 121.6, 110.0, 50.7, 42.2, 39.9; HRMS (ESI-TOF): calc. for $C_{23}H_{15}BrO_2$ $[M+H]^+$ 403.0327, found 403.0323.

1-(4-bromophenyl)-1a-(*p*-tolyl)-5-(trifluoromethyl)-1a,7a-dihydro-1*H*cyclopropa[*b*]



naphthalene-2,7-dione (2t) White solid (25 mg, yield 52%), mp 197-200 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 8.44 (s, 1H), 8.26 (d, *J* = 8.1 Hz, 1H), 8.04 (d, *J* = 9.6 Hz, 1H), 7.26 (d, *J* = 8.5 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.65 (d, *J* = 8.5 Hz, 2H), 3.65 (d, *J* = 5.6 Hz, 1H), 3.36 (d, *J* = 5.6 Hz, 1H), 2.34 (s, 3H);^{13}C NMR (125 MHz, $CDCl_3$) δ_C = 191.2, 189.6, 138.4, 134.8 (q, $^{2}J_{C\text{-}F}$ = 21.2 Hz), 133.0, 132.3, 132.1, 131.5, 131.3, 130.6 (q, $^{3}J_{C\text{-}F}$ = 3.5 Hz), 129.6, 129.2, 128.6 (q, $^{1}J_{C\text{-}F}$ = 267.1 Hz), 127.8, 125.4 (q, $^{3}J_{C\text{-}F}$ = 3.7 Hz), 121.9, 50.8, 42.0, 40.3, 21.2; ^{19}F NMR (470 MHz, $CDCl_3$) δ_F = -63.4 (s,1F). HRMS (ESI-TOF): calc. for $C_{25}H_{16}BrF_3O_2$ $[M+H]^+$ 485.0358, found 485.0350.

(*E*)-7-(hydroxyimino)-1,7a-di-*p*-tolyl-1,1a,7,7a-tetrahydro-2*H*-cyclopropa[*b*]naphthalen-2-



one (3g) White solid (32 mg, yield 87%), mp 192-195 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 9.59 (s, 1H), 8.20 (d, *J* = 7.9 Hz, 1H), 8.06 (d, *J* = 7.9 Hz, 1H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 6.94 (d, *J* = 8.2 Hz, 2H), 6.78 (d, *J* = 8.2 Hz, 2H), 4.41 (d, *J* = 6.0 Hz, 1H), 3.09 (d, *J* = 6.0 Hz, 1H), 2.31 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C = 192.8, 152.0, 137.3, 136.7, 133.7, 132.4, 131.8, 131.2, 130.6, 130.1, 129.8, 128.8, 128.7, 128.5, 128.2, 124.1, 48.4, 39.1, 25.6, 21.2, 21.0; HRMS (ESI-TOF): calc. for $C_{25}H_{21}NO_2$ $[M+H]^+$ 368.1644, found 368.1649.

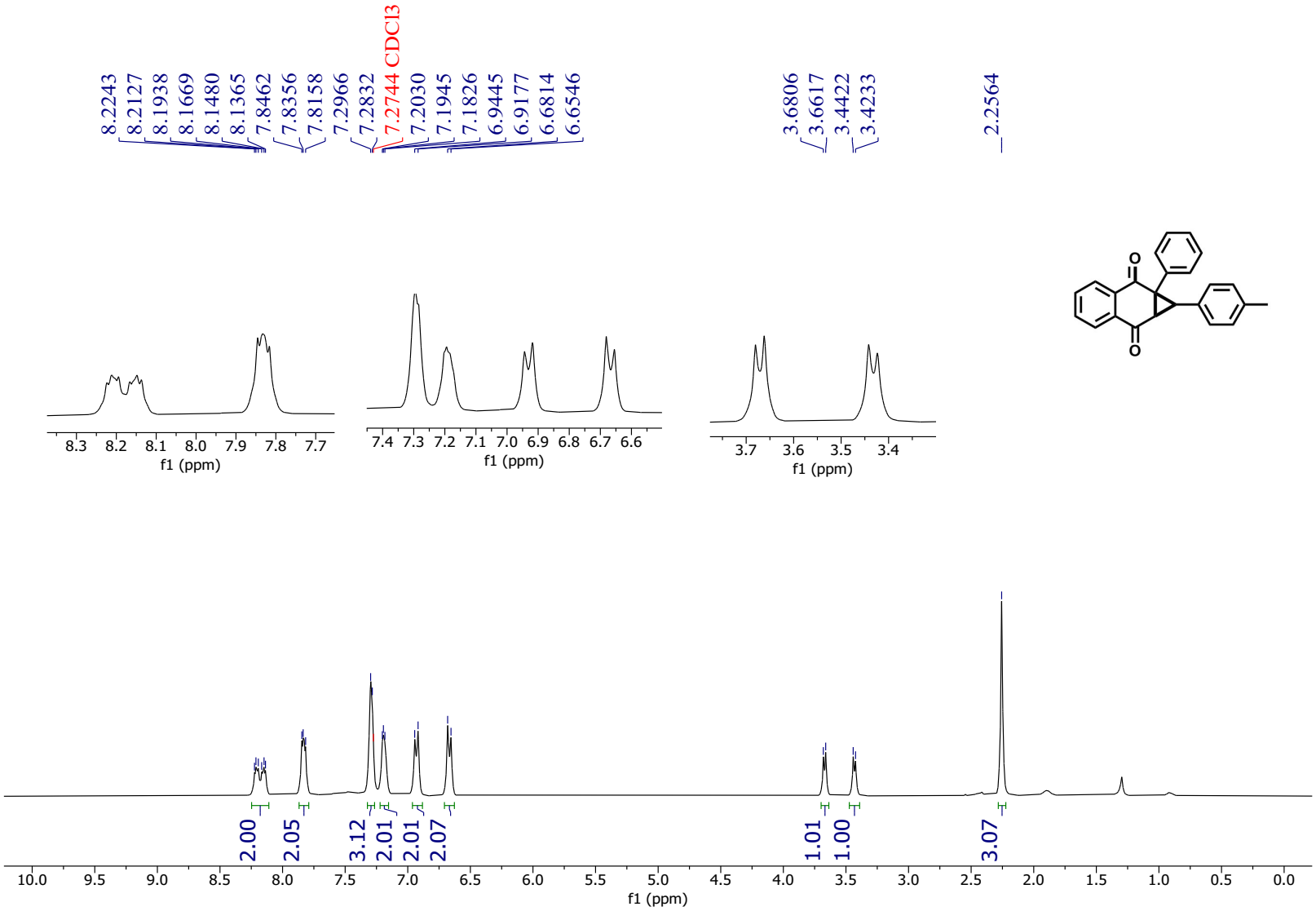
2. References

1. (a) L. Zheng, B. Zhou, H. Jin, T. Li and Y. Liu, *Org. Lett.* 2018, **20**, 7053-7056; (b) L. Zheng, H. Xue, B. Zhou, S. P. Luo, H. Jin and Y. Liu, *Org. Lett*. 2021, **22**, 4478-4482; (c) Y. -N. Wu, R. Fu, N. -N.Wang, W. -J. Hao, G. Li, S. -J. Tu and B. Jiang, *J. Org. Chem.* 2016, **81**, 4762-4770; (d) M. Mandal and R. Balamurugan, *Adv. Synth. Catal*. 2018, **360**, 1453-1465.

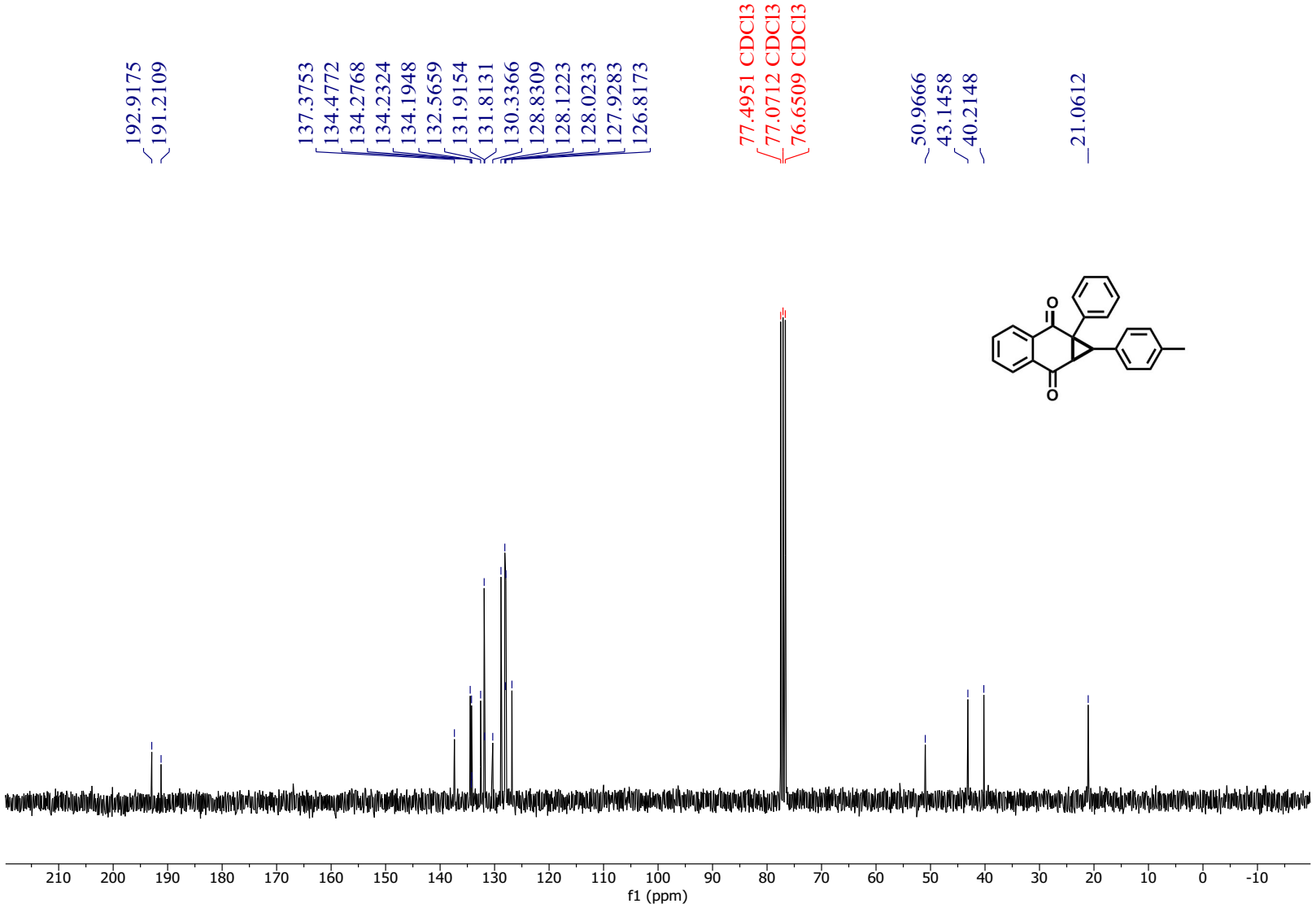
2. Y. S. Hosseini Nasab, S. Rajai-Daryasarei, F. Rominger and S. Balalaie, *J. Org. Chem.* 2024, **89**, 13575-13584.

3. ^{1}H, ^{13}C NMR and ^{19}F NMR spectra of products

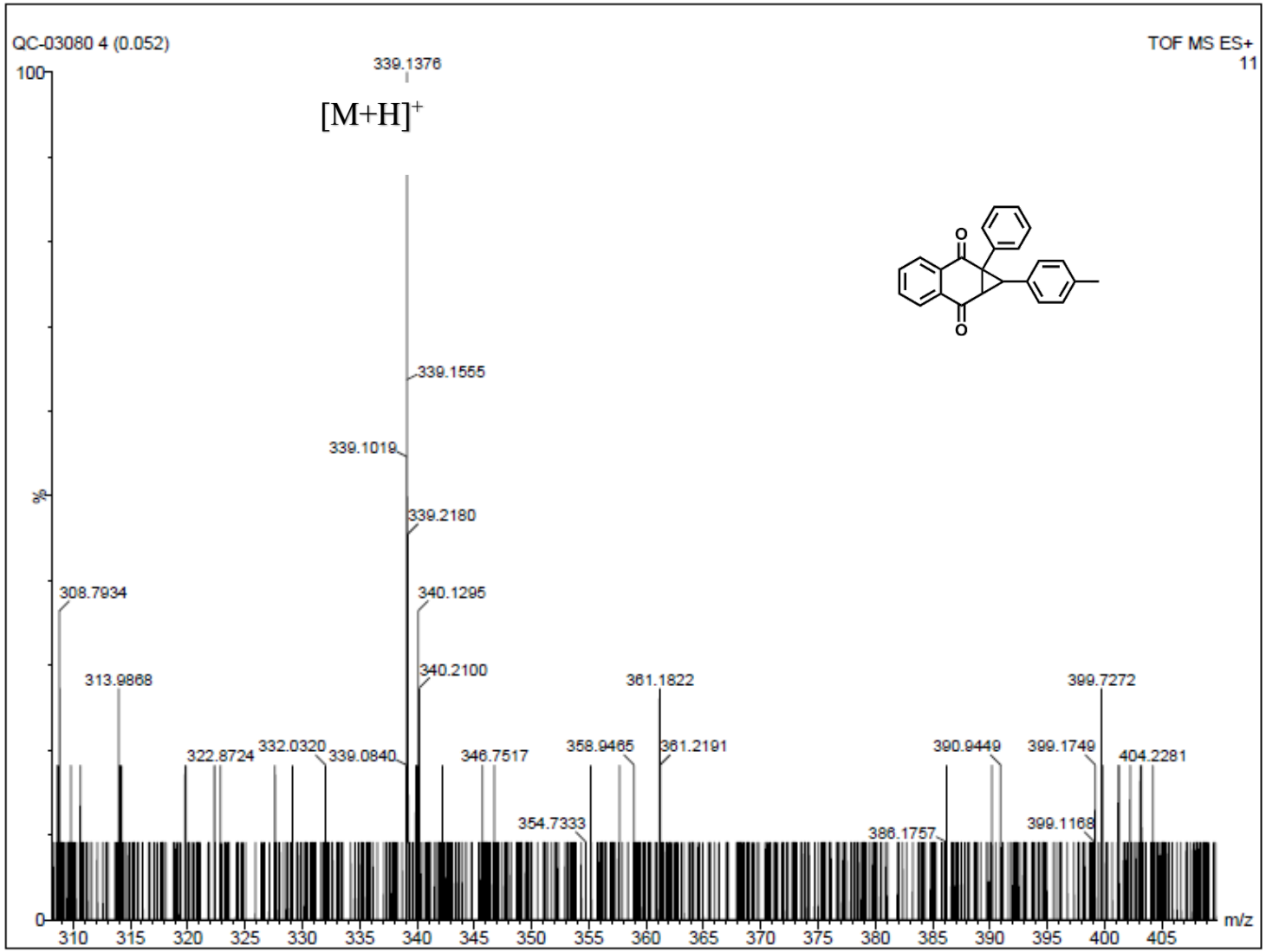
^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **2a**



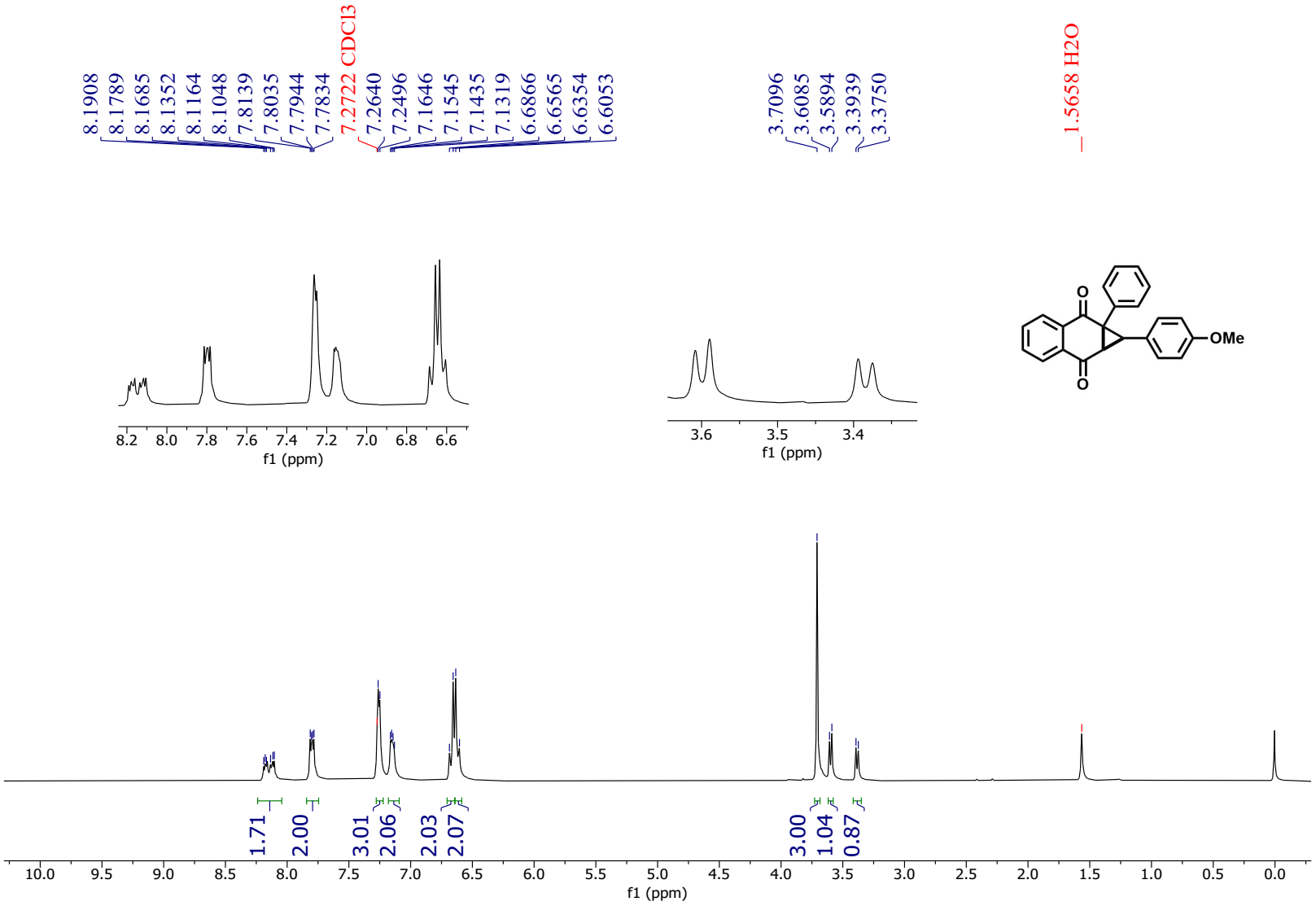
^{13}C NMR (75 MHz, $CDCl_3$) spectrum of **2a**



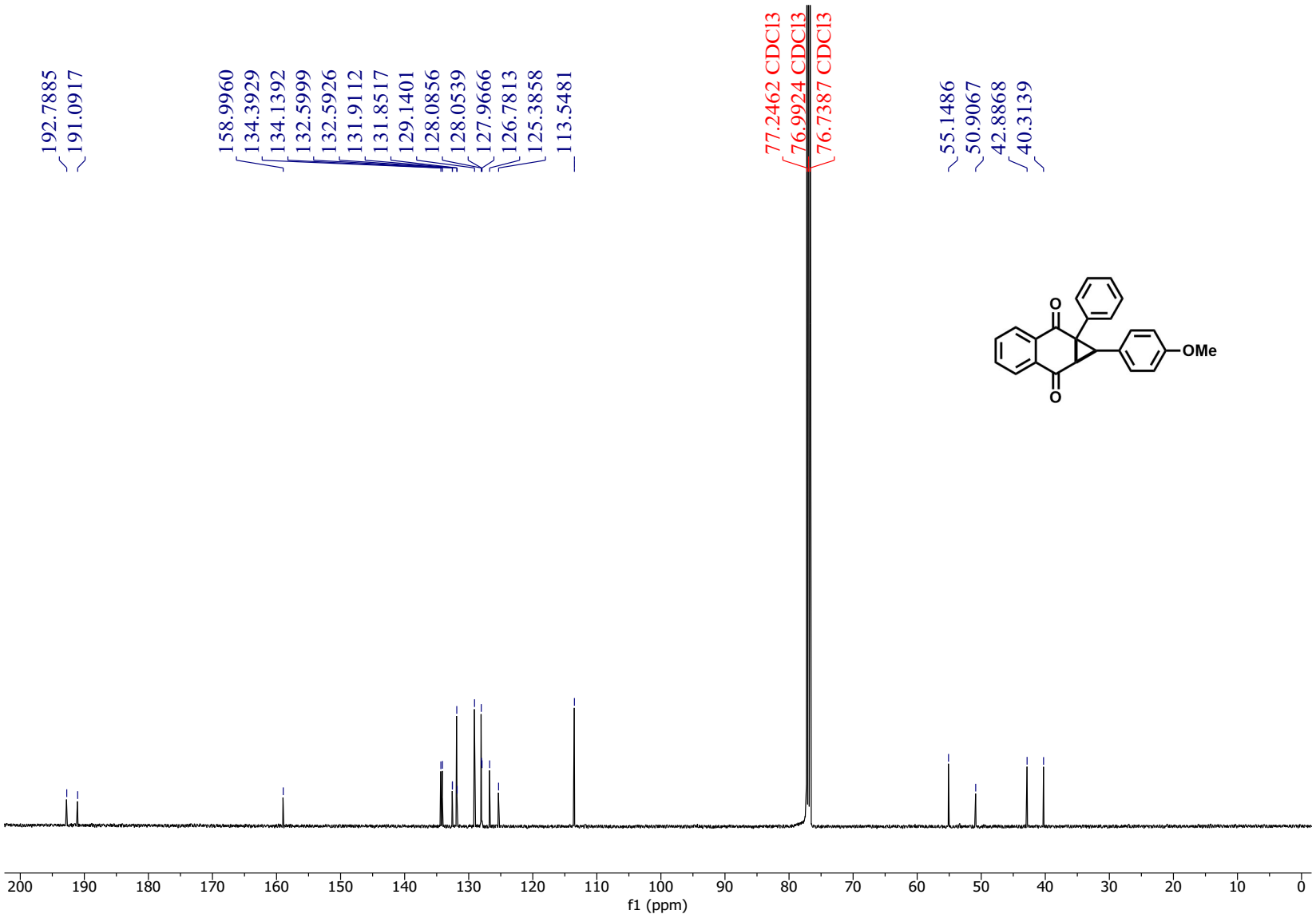
HRMS-ESI Compound **2a**



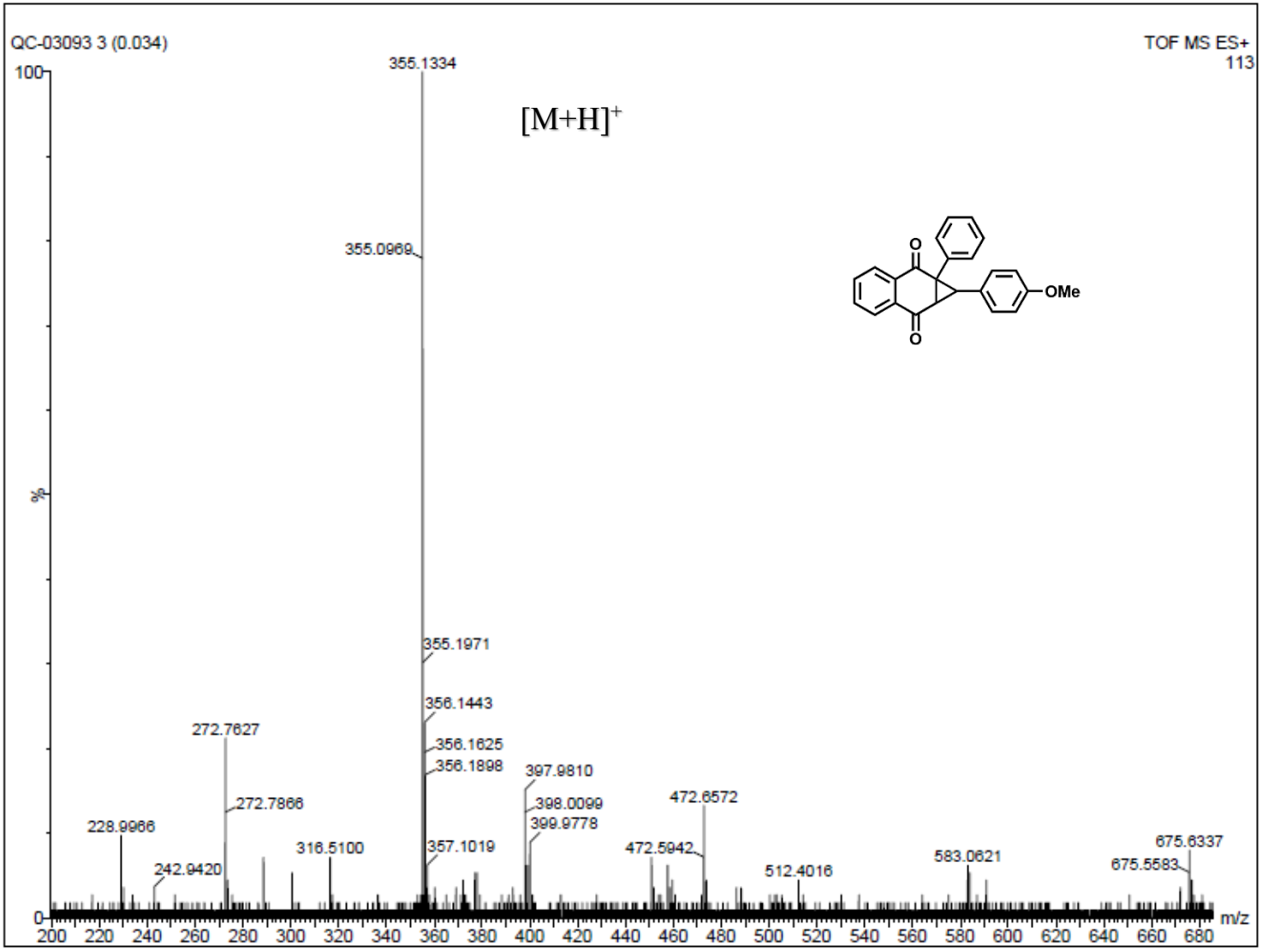
^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **2b**



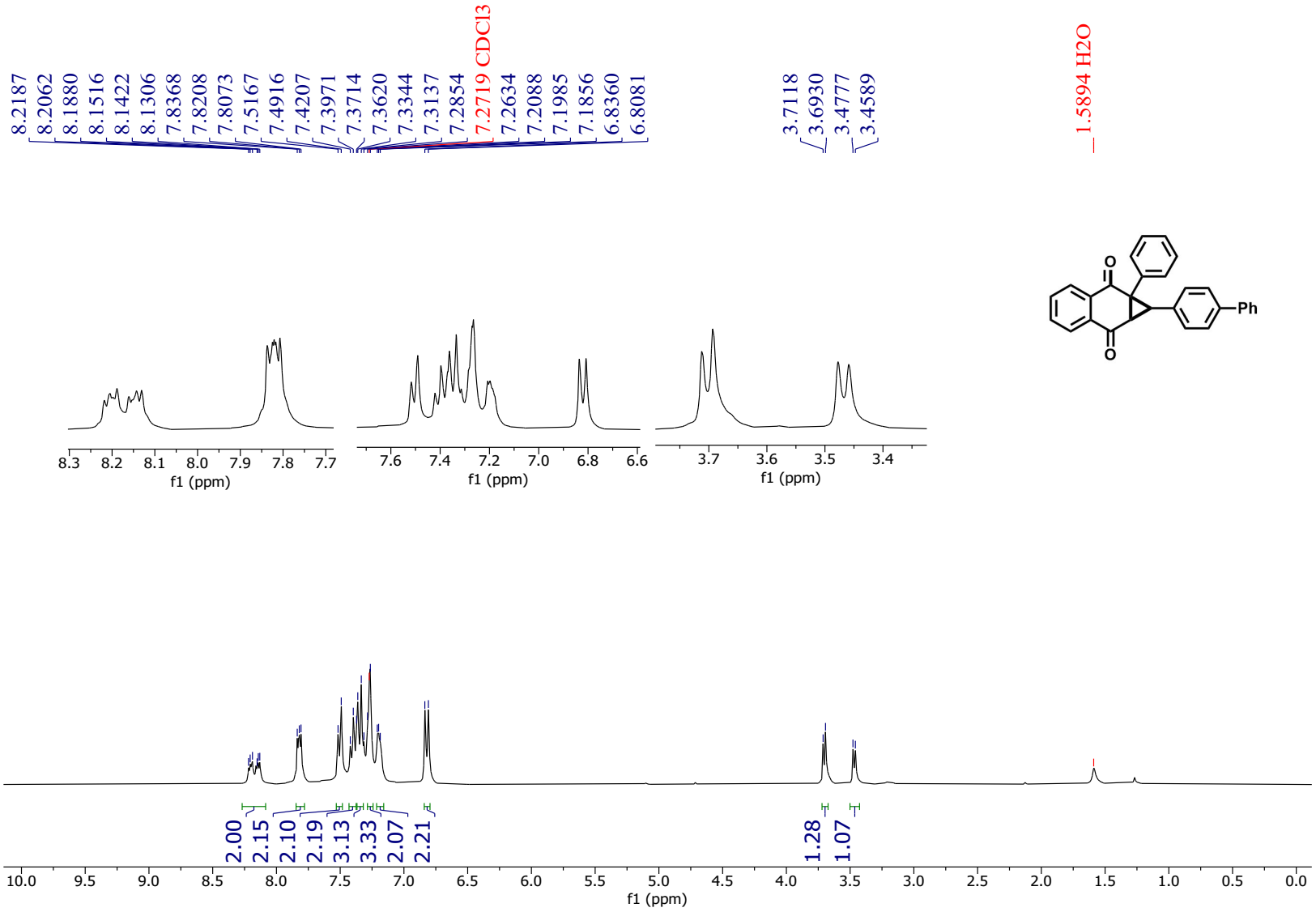
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **2b**



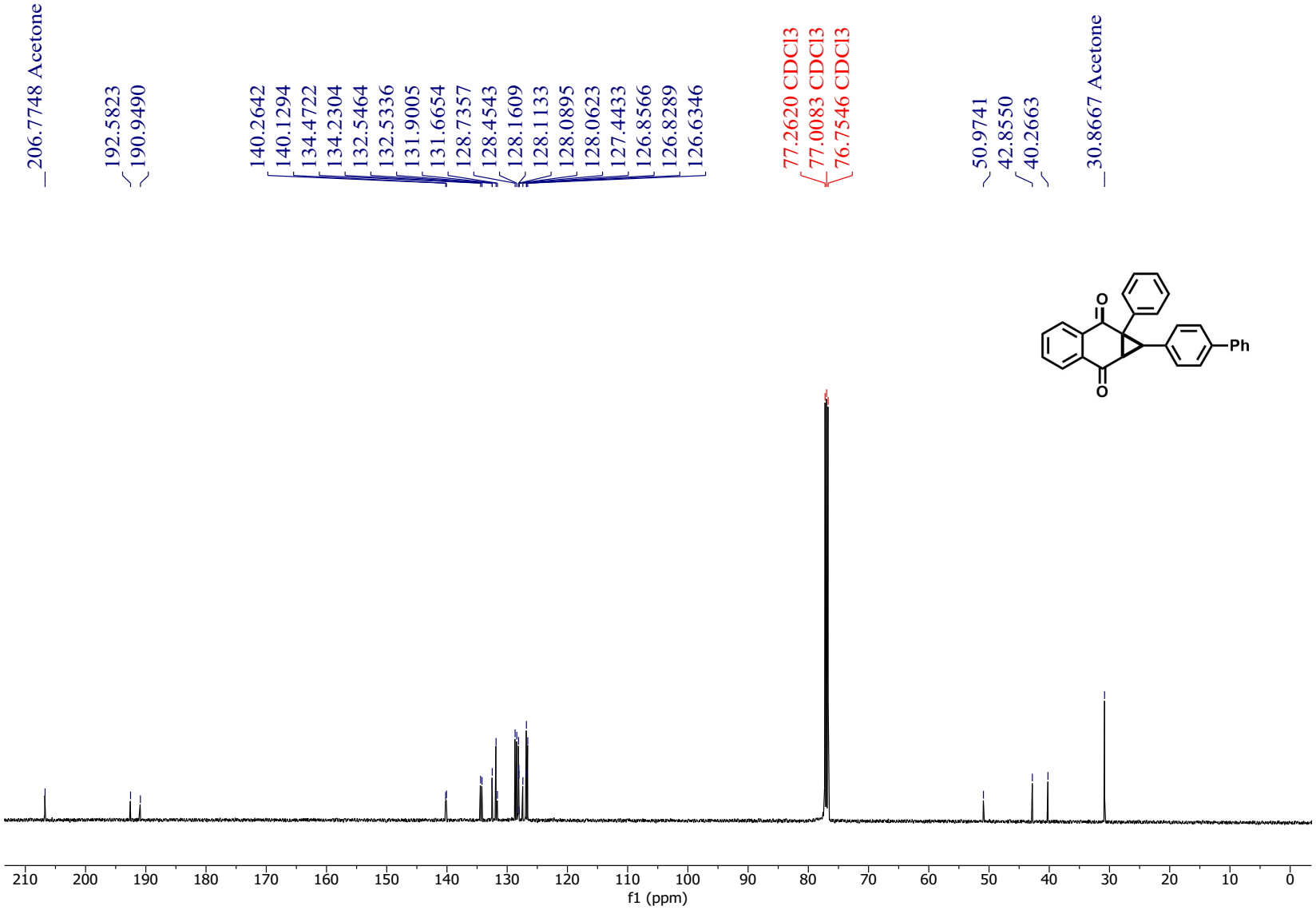
HRMS-ESI Compound **2b**



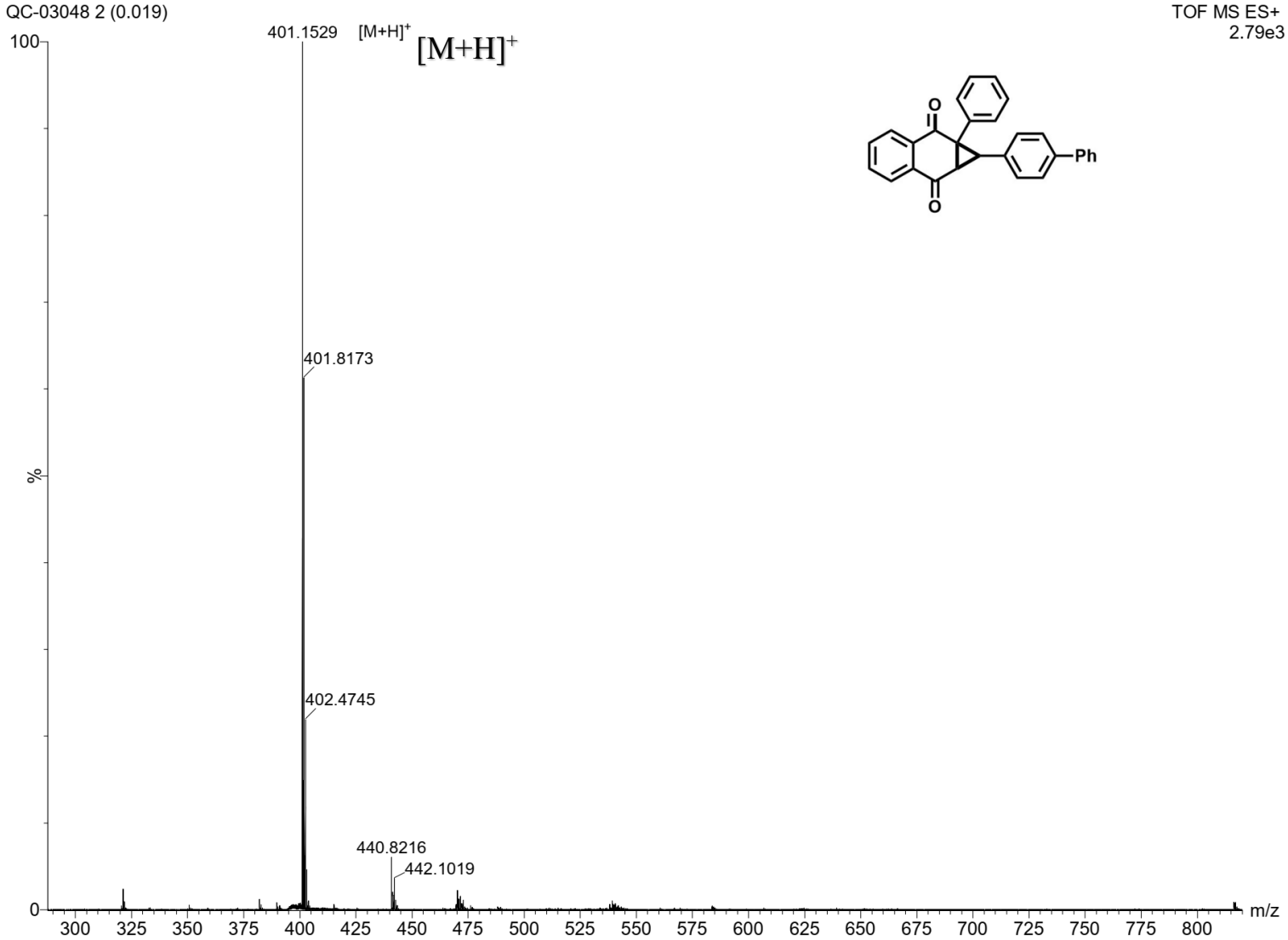
^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **2c**



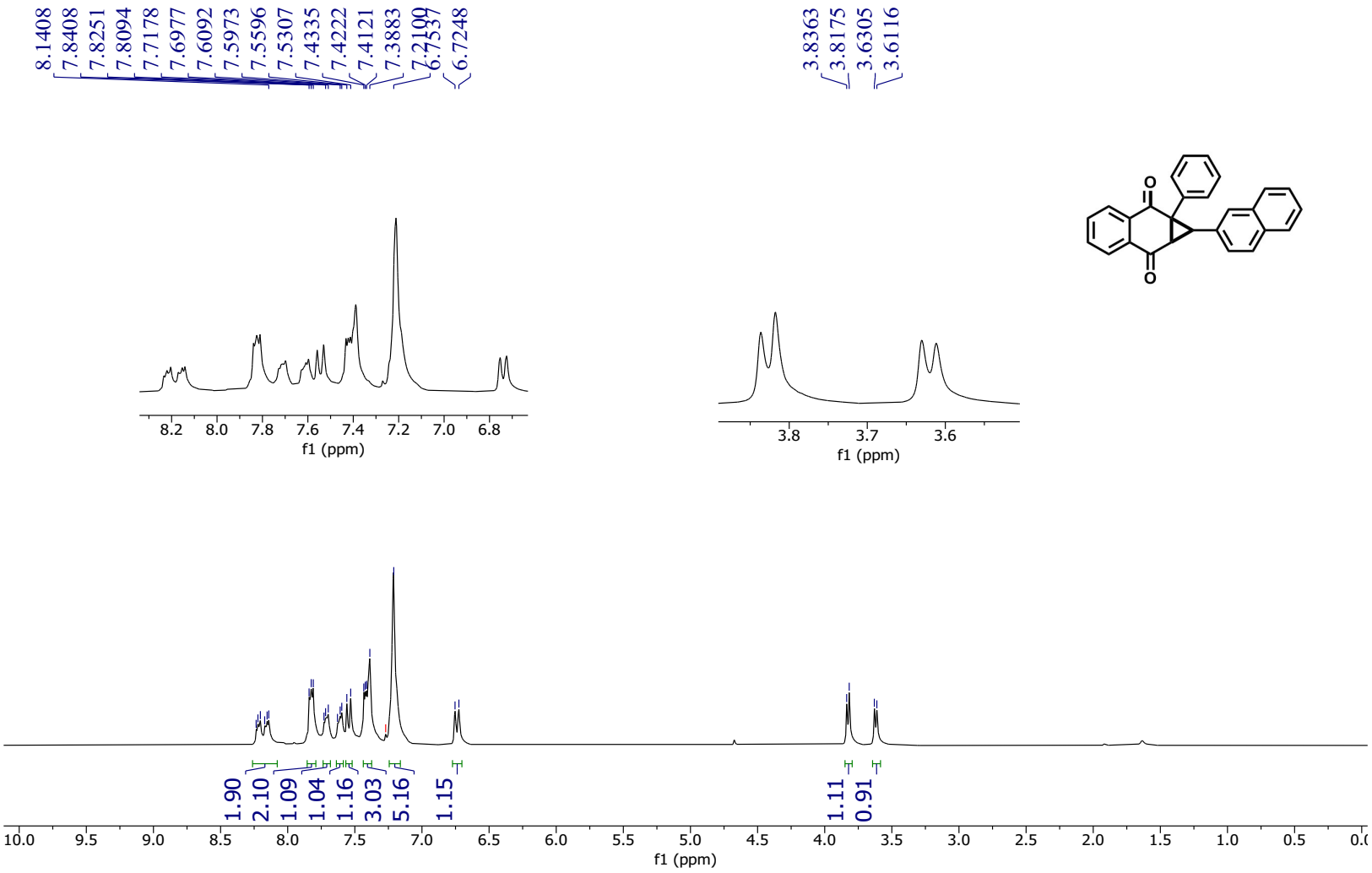
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **2c**



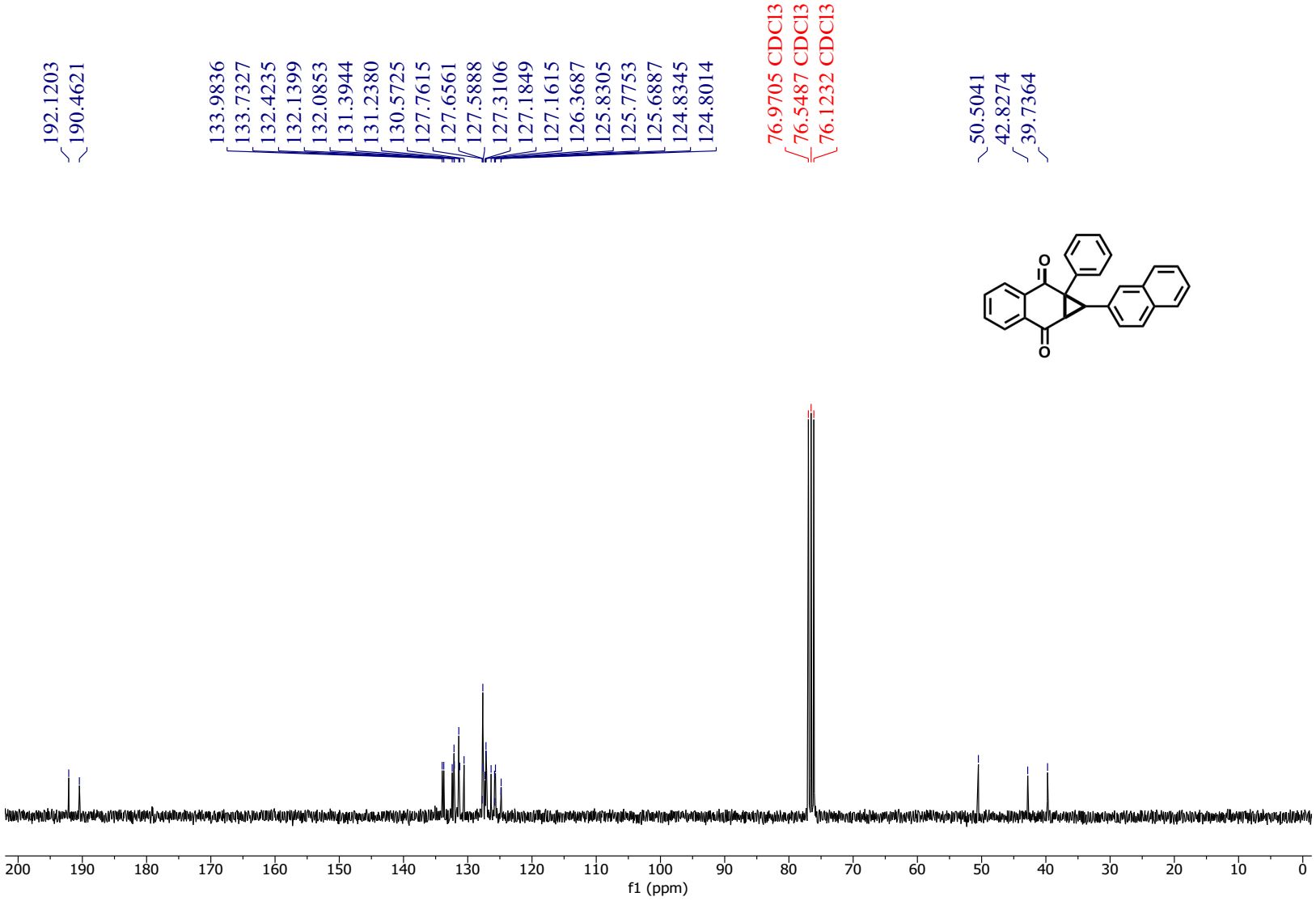
HRMS-ESI Compound **2c**



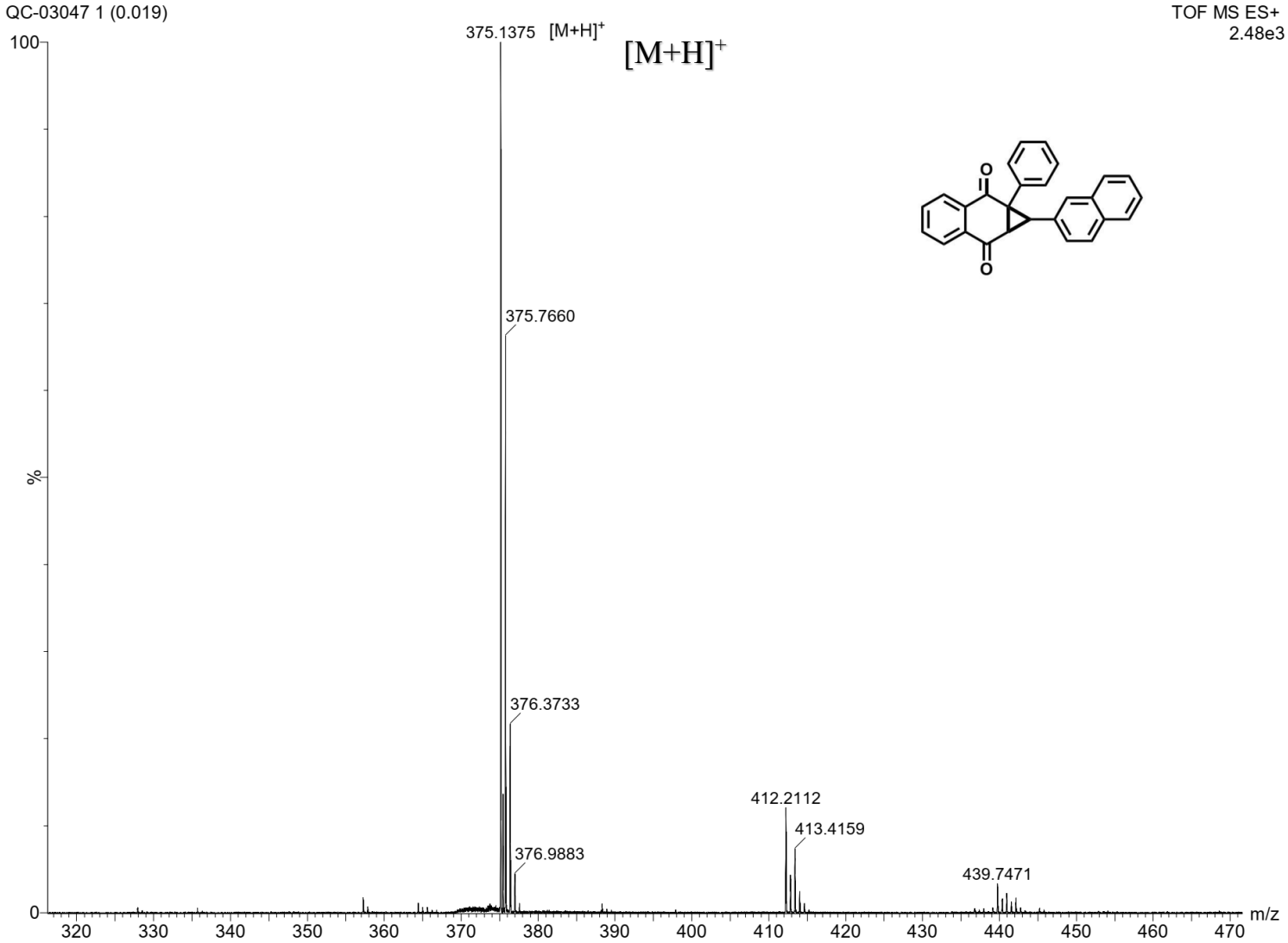
^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **2d**



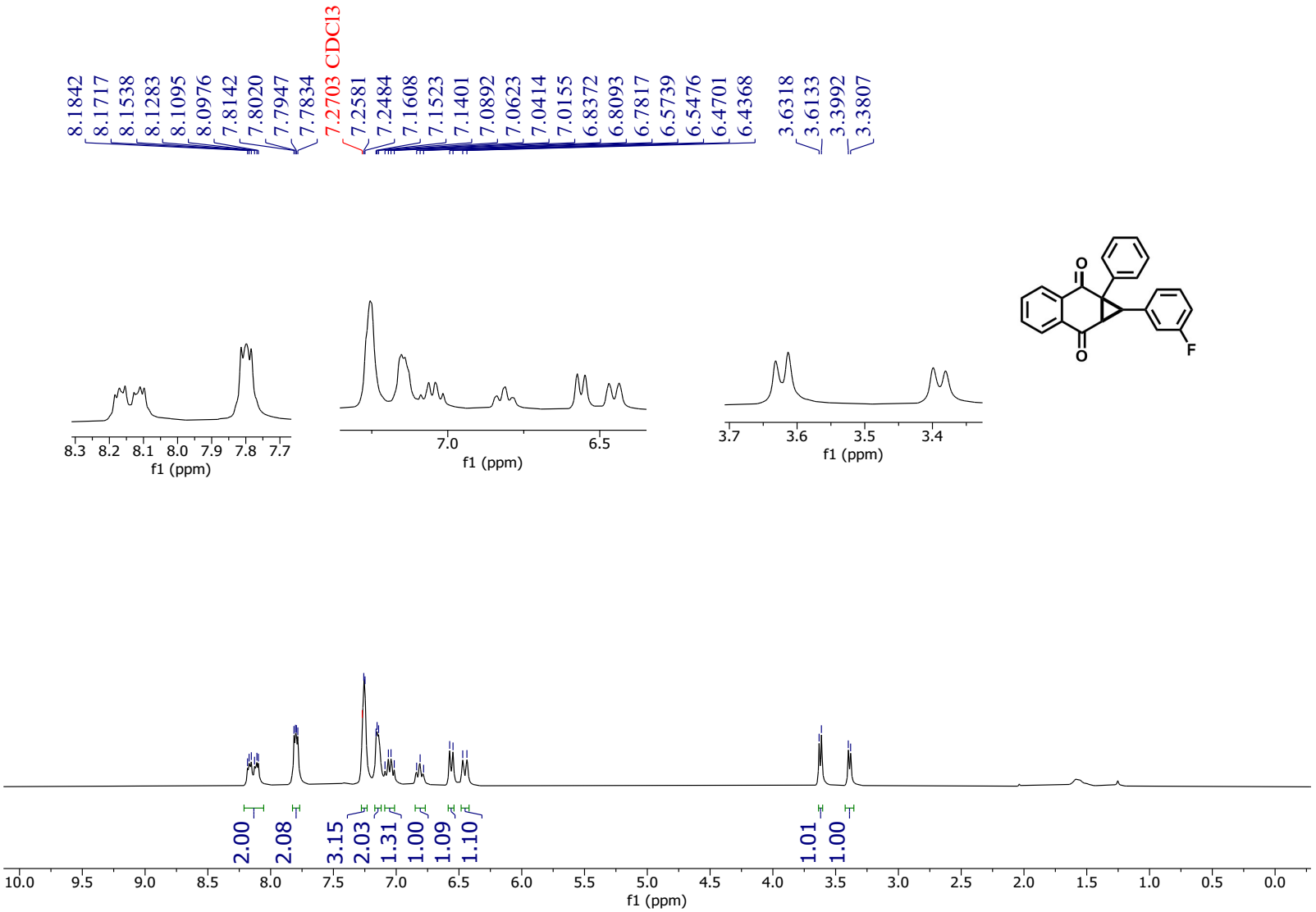
^{13}C NMR (75 MHz, $CDCl_3$) spectrum of **2d**



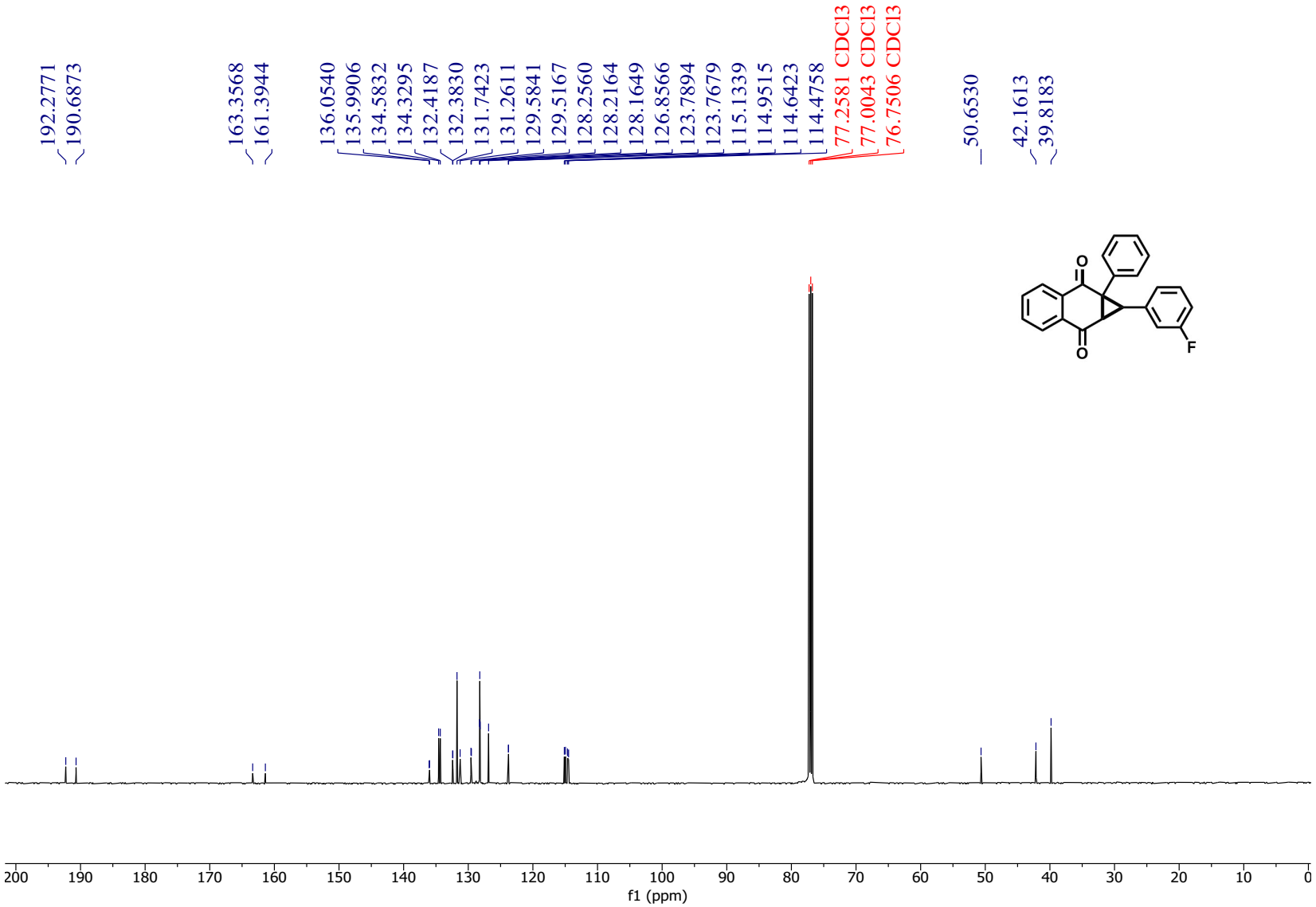
HRMS-ESI Compound **2d**



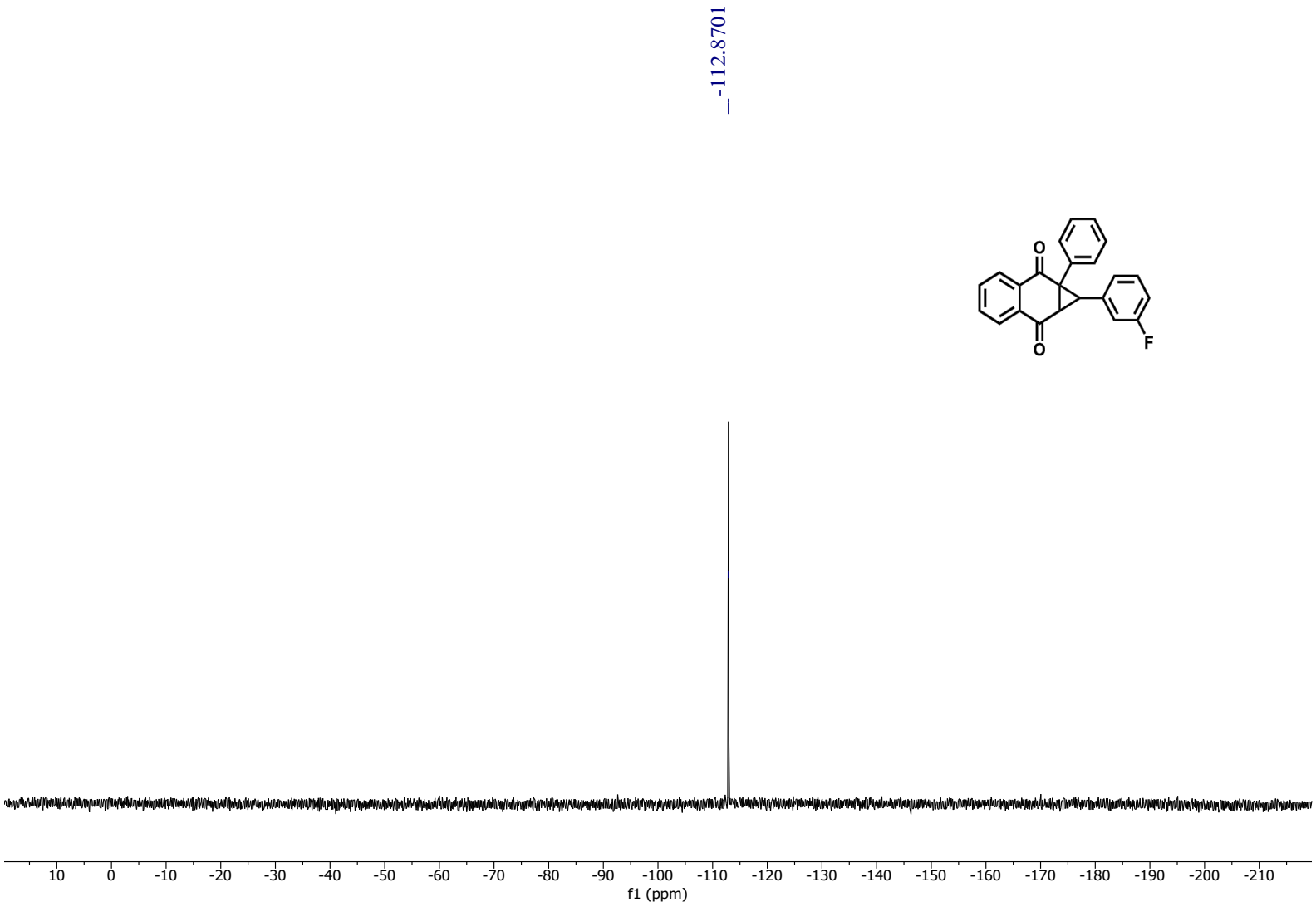
^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **2e**



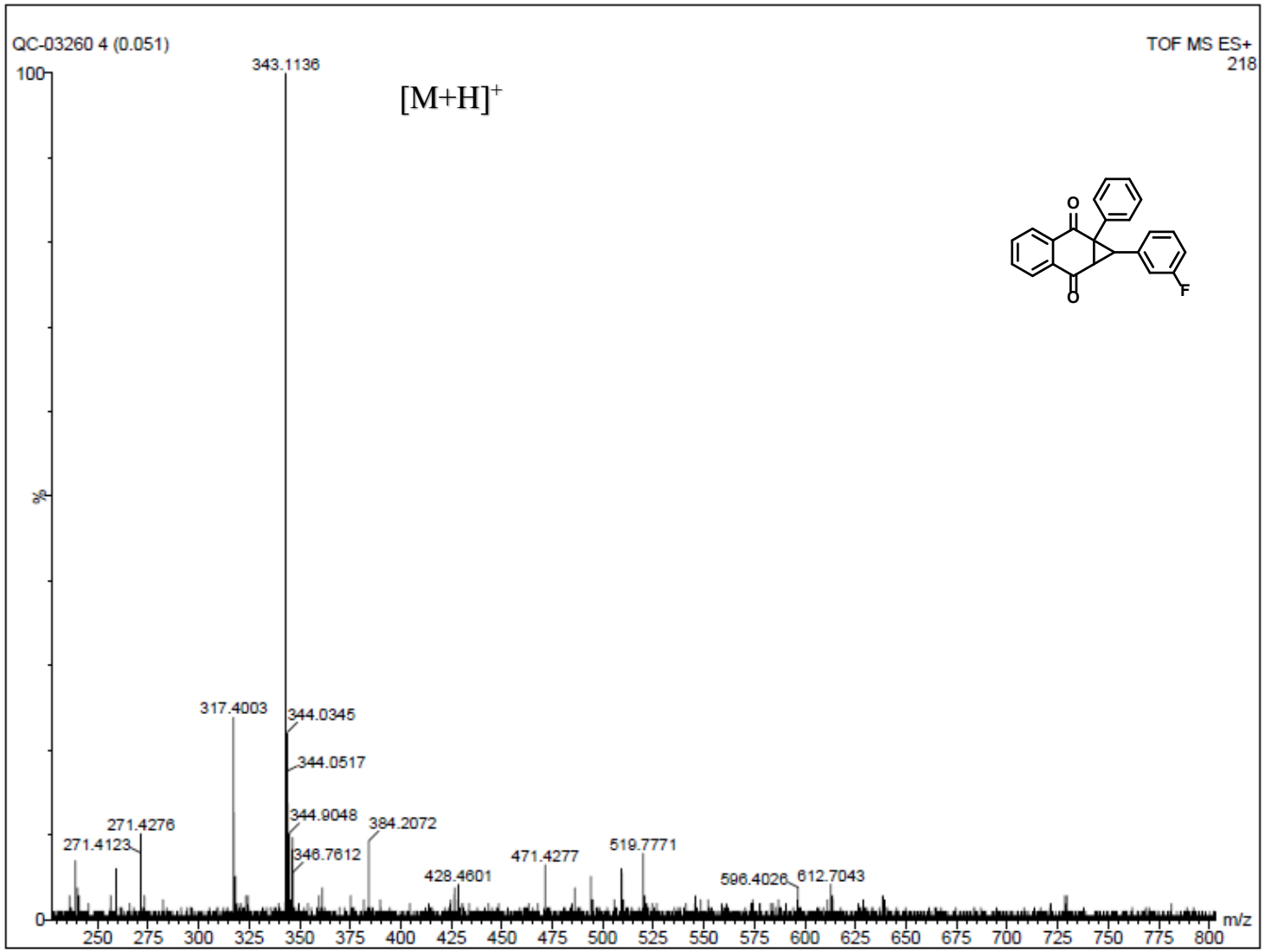
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **2e**



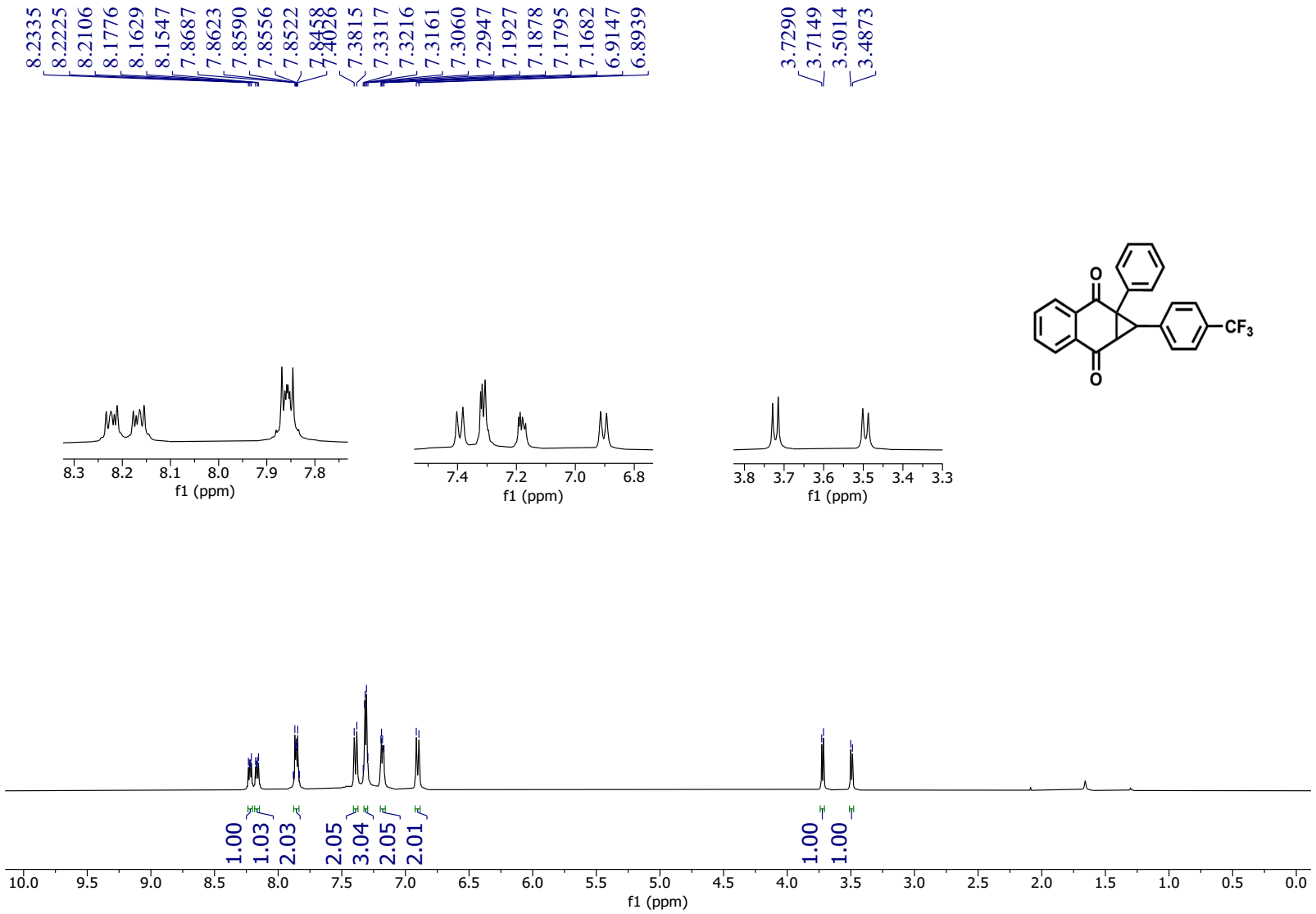
^{19}F NMR (282 MHz, $CDCl_3$) spectrum of **2e**



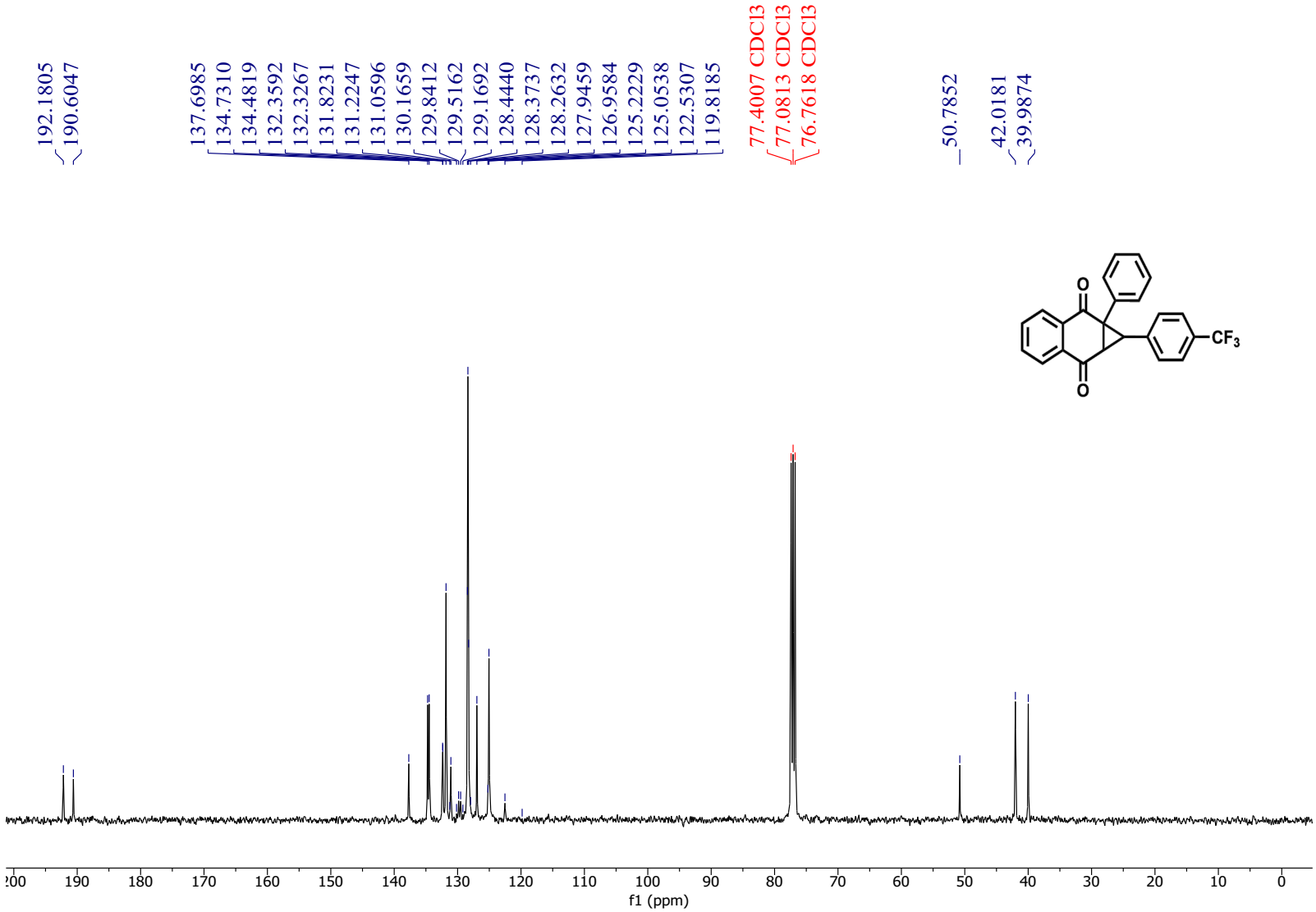
HRMS-ESI Compound **2e**



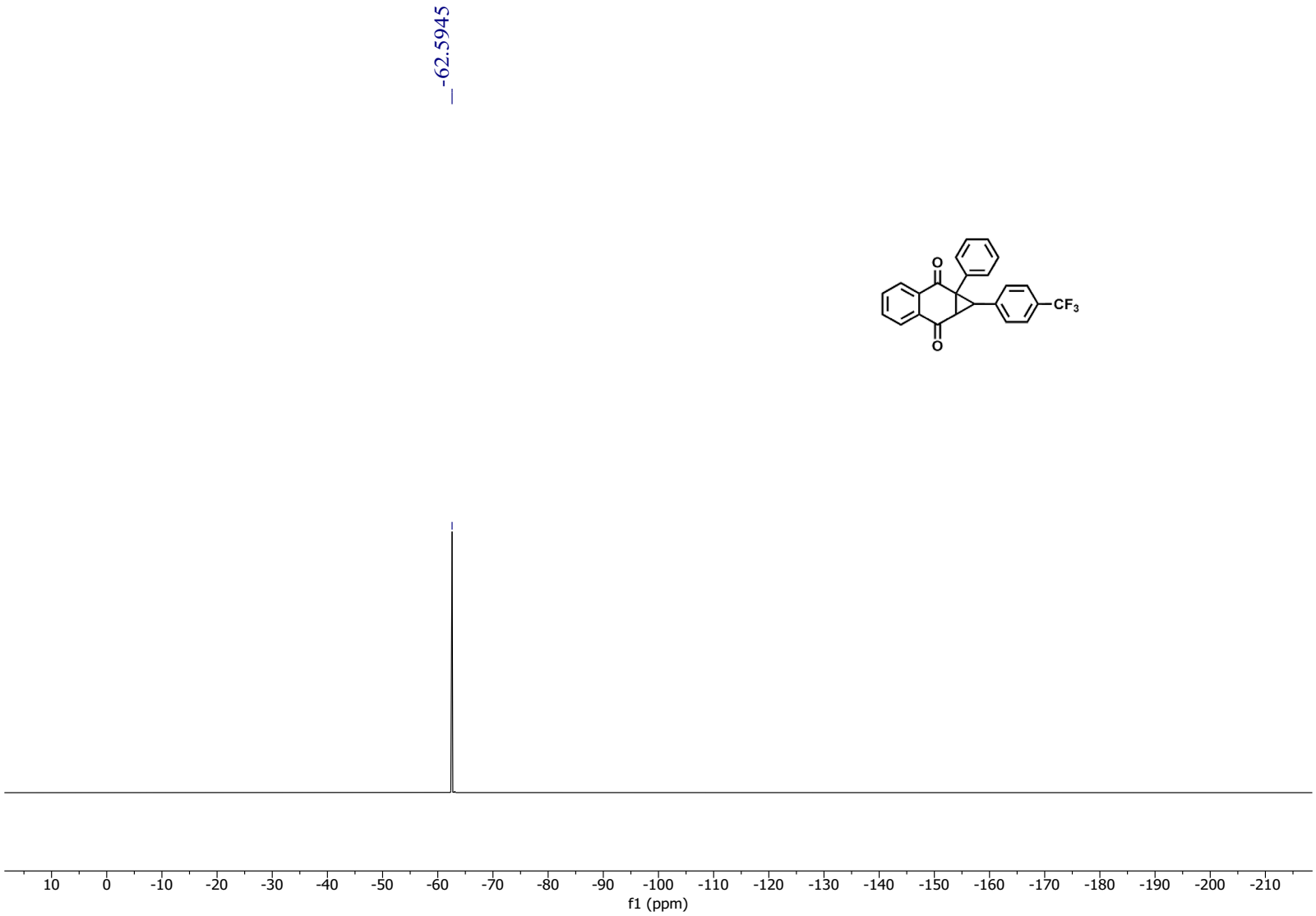
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2f**



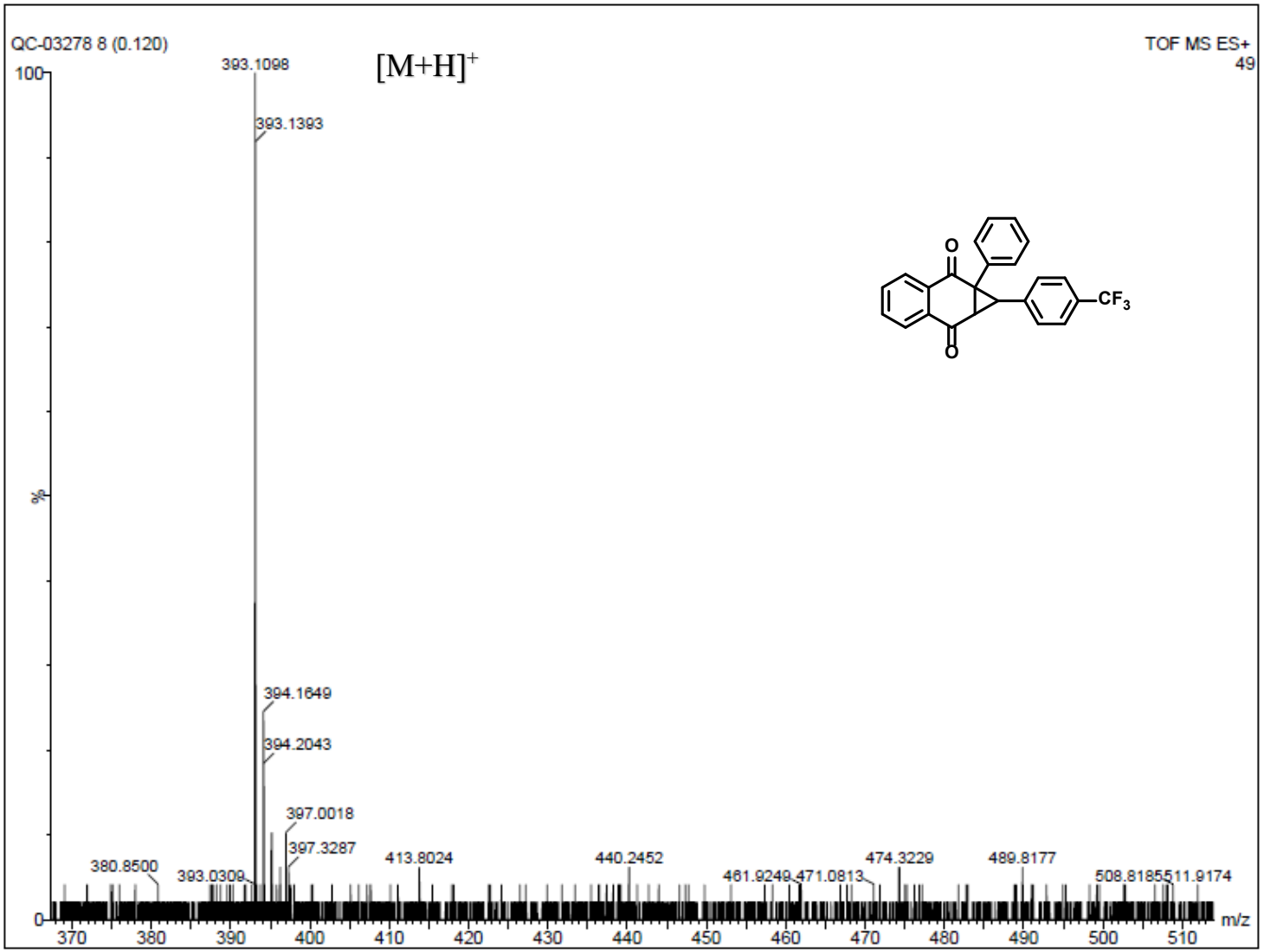
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2f**



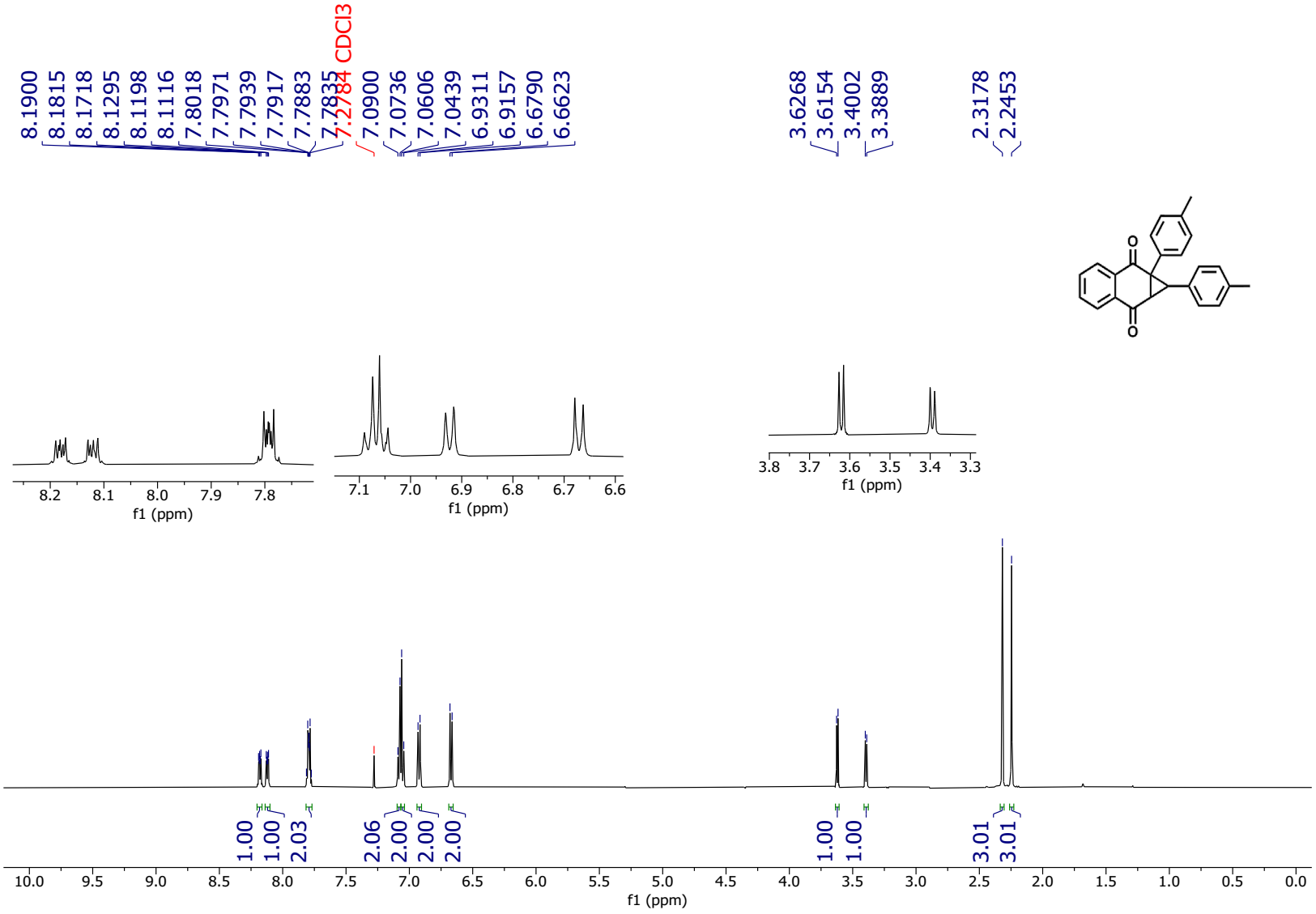
^{19}F NMR (377 MHz, $CDCl_3$) spectrum of **2f**



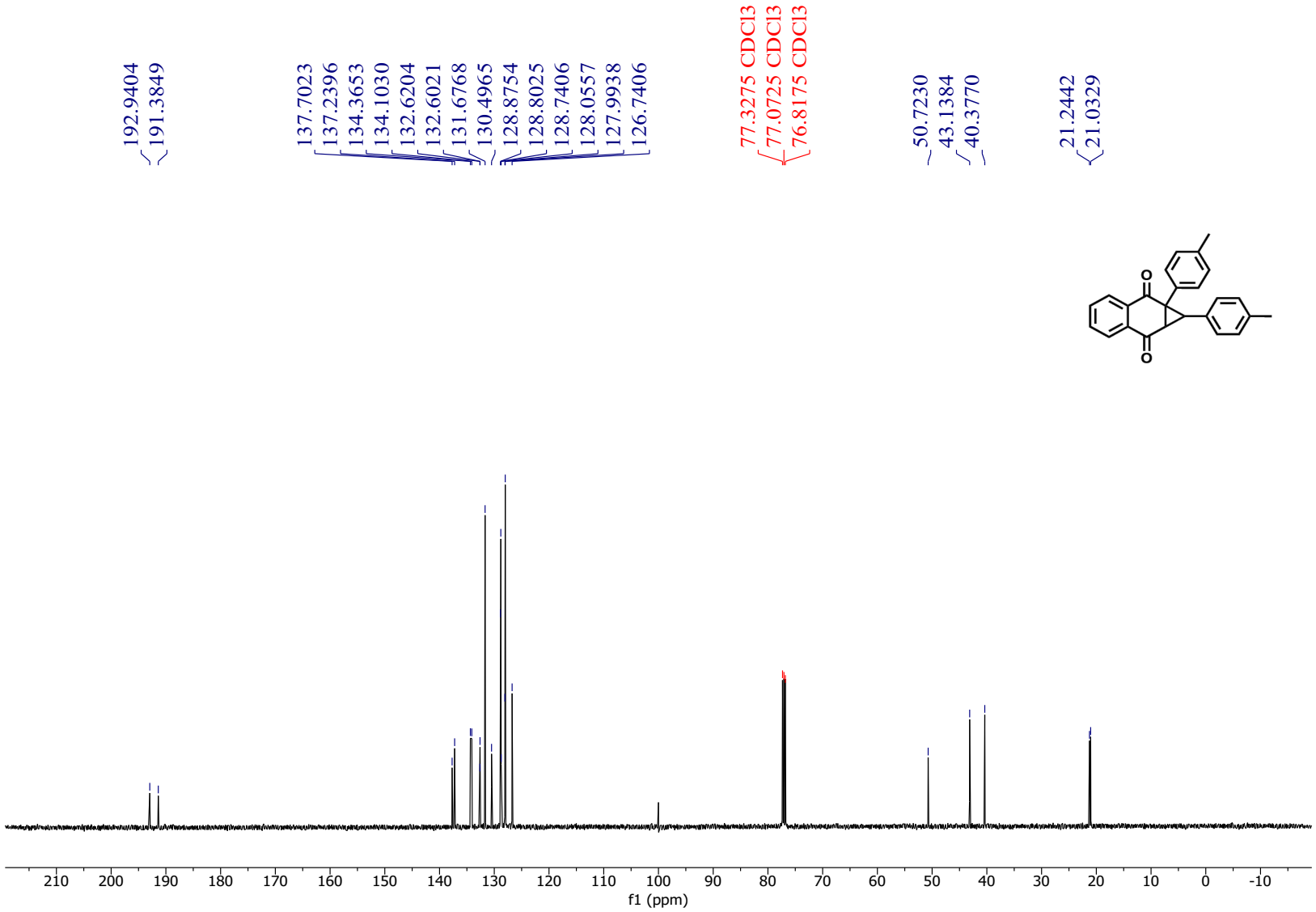
HRMS-ESI Compound **2f**



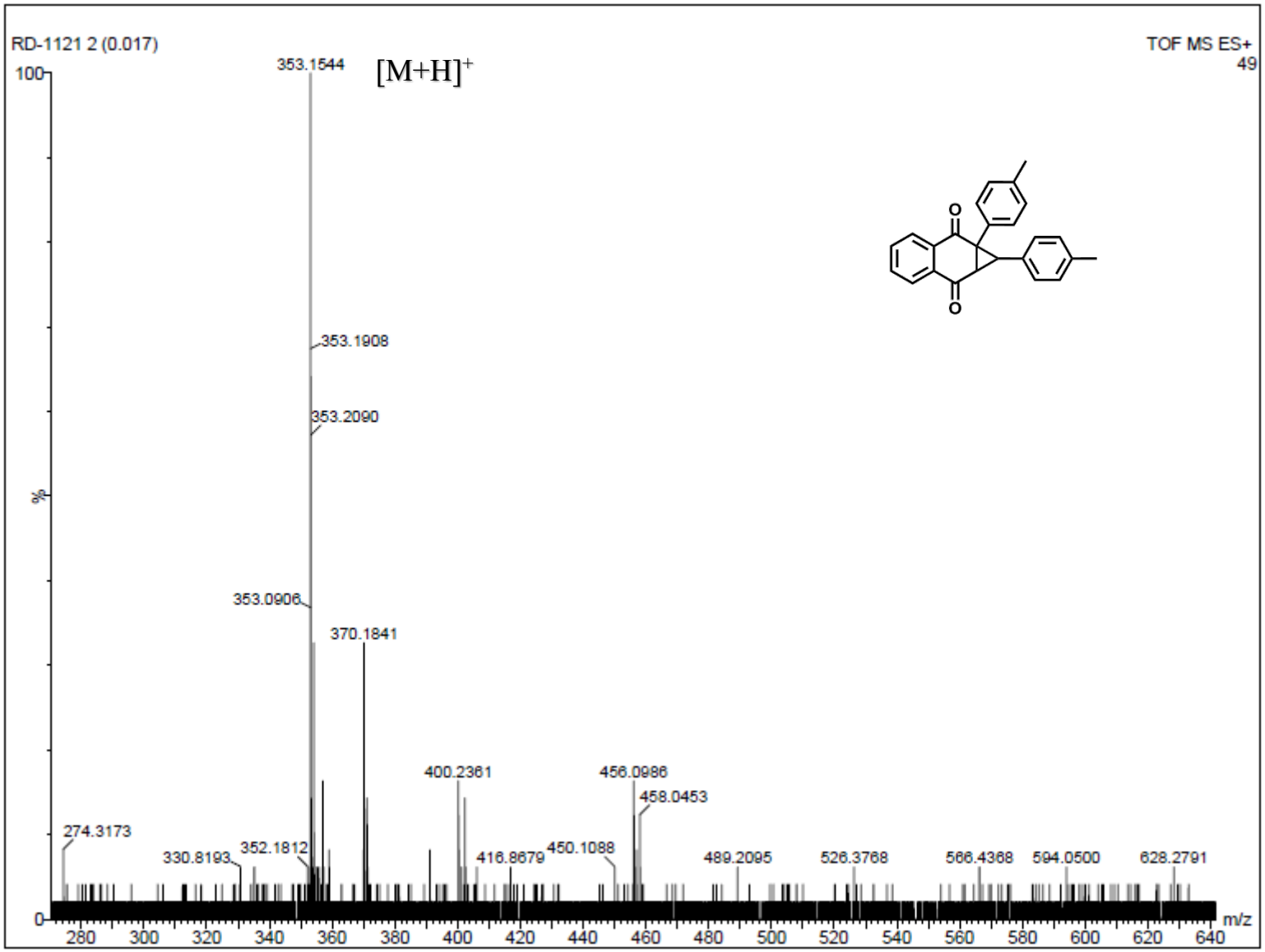
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2g**



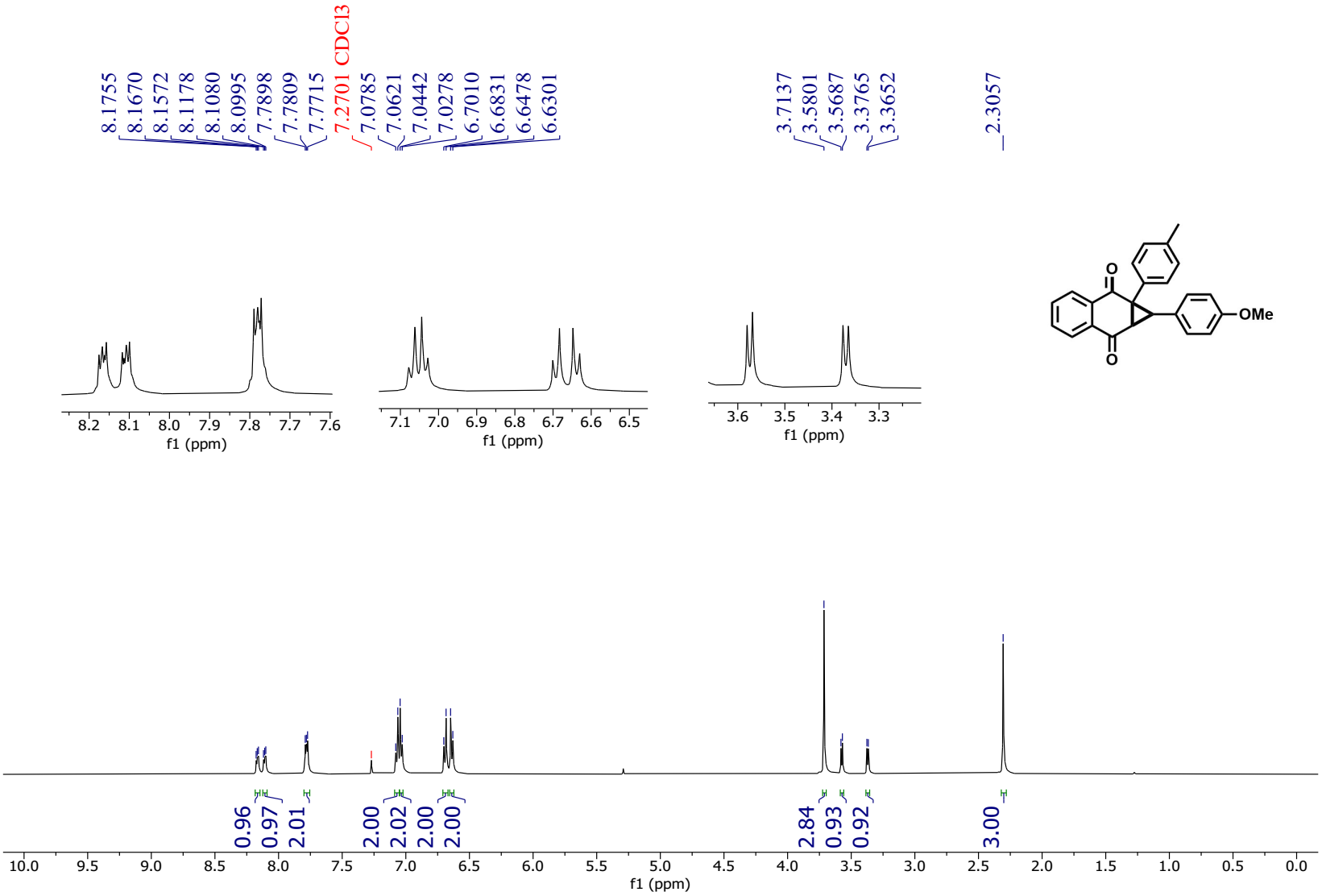
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **2g**



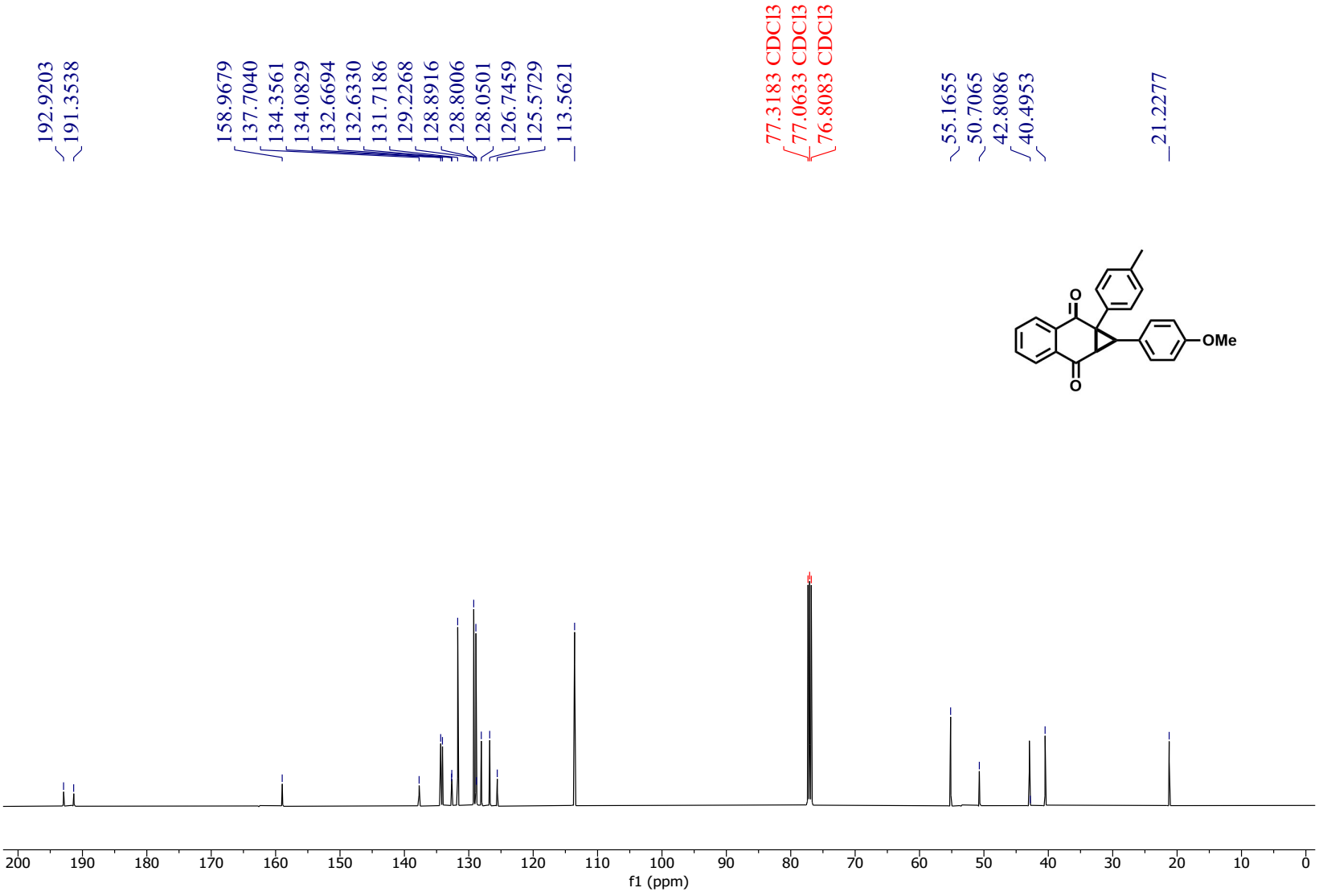
HRMS-ESI Compound **2g**



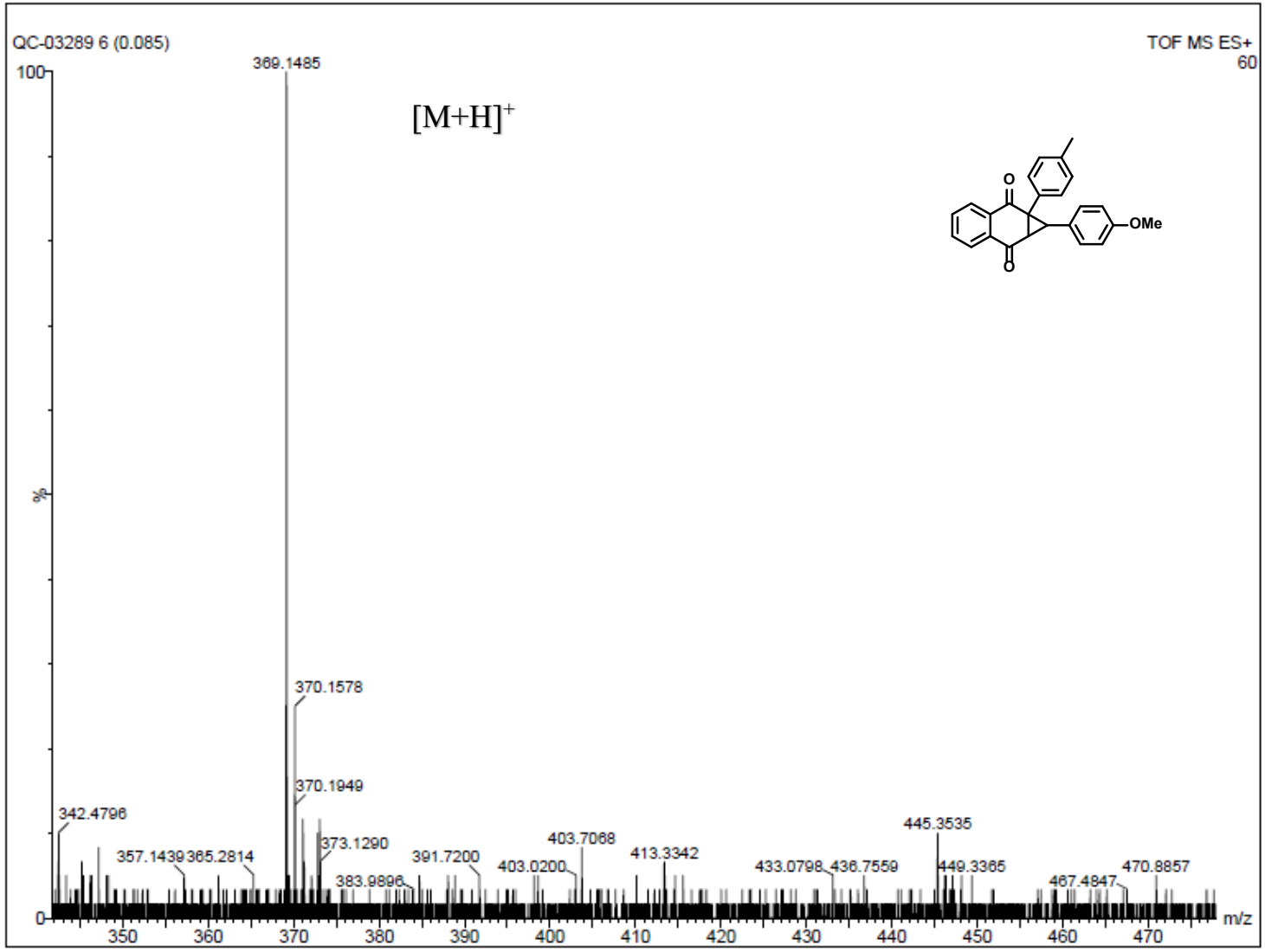
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2h**



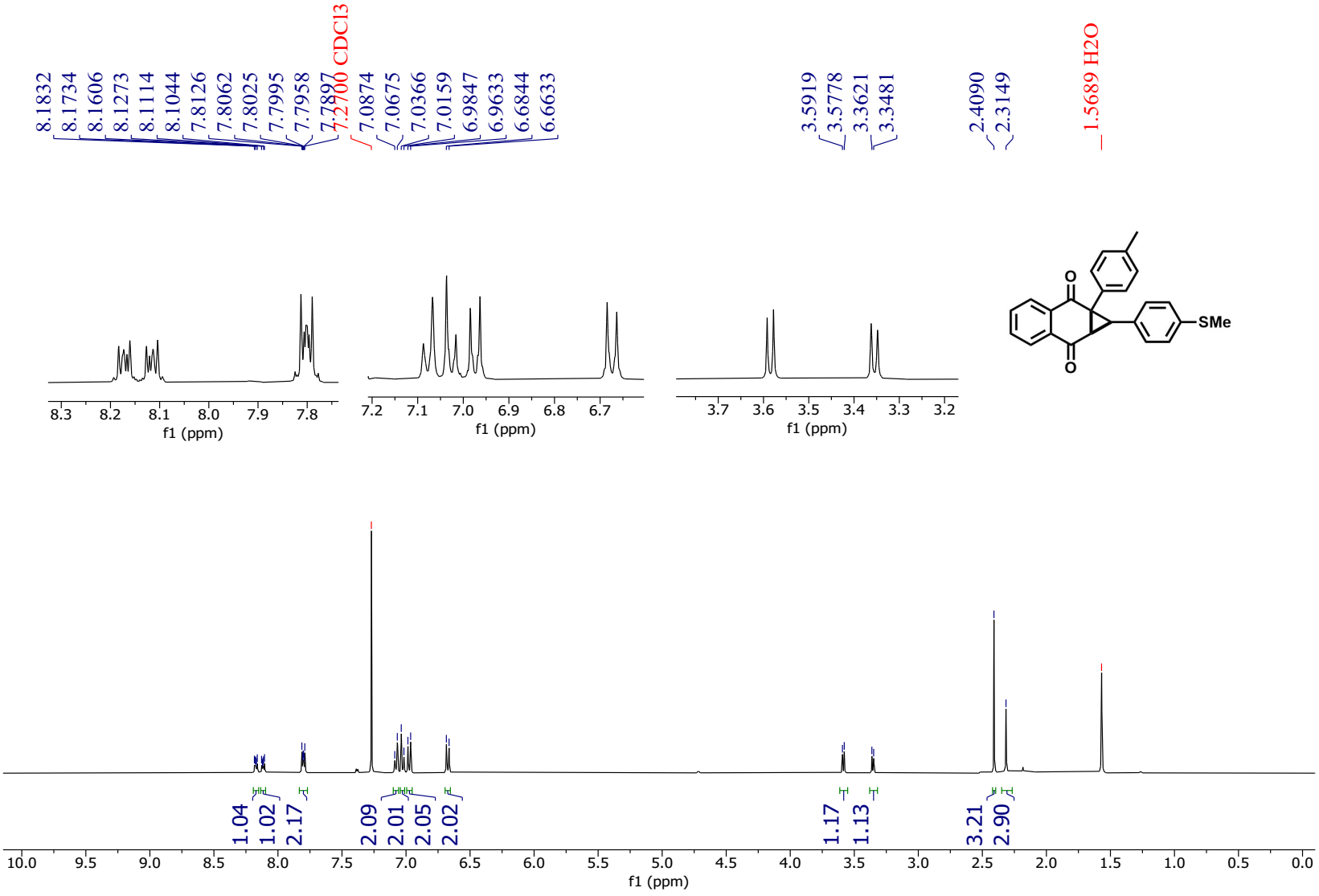
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **2h**



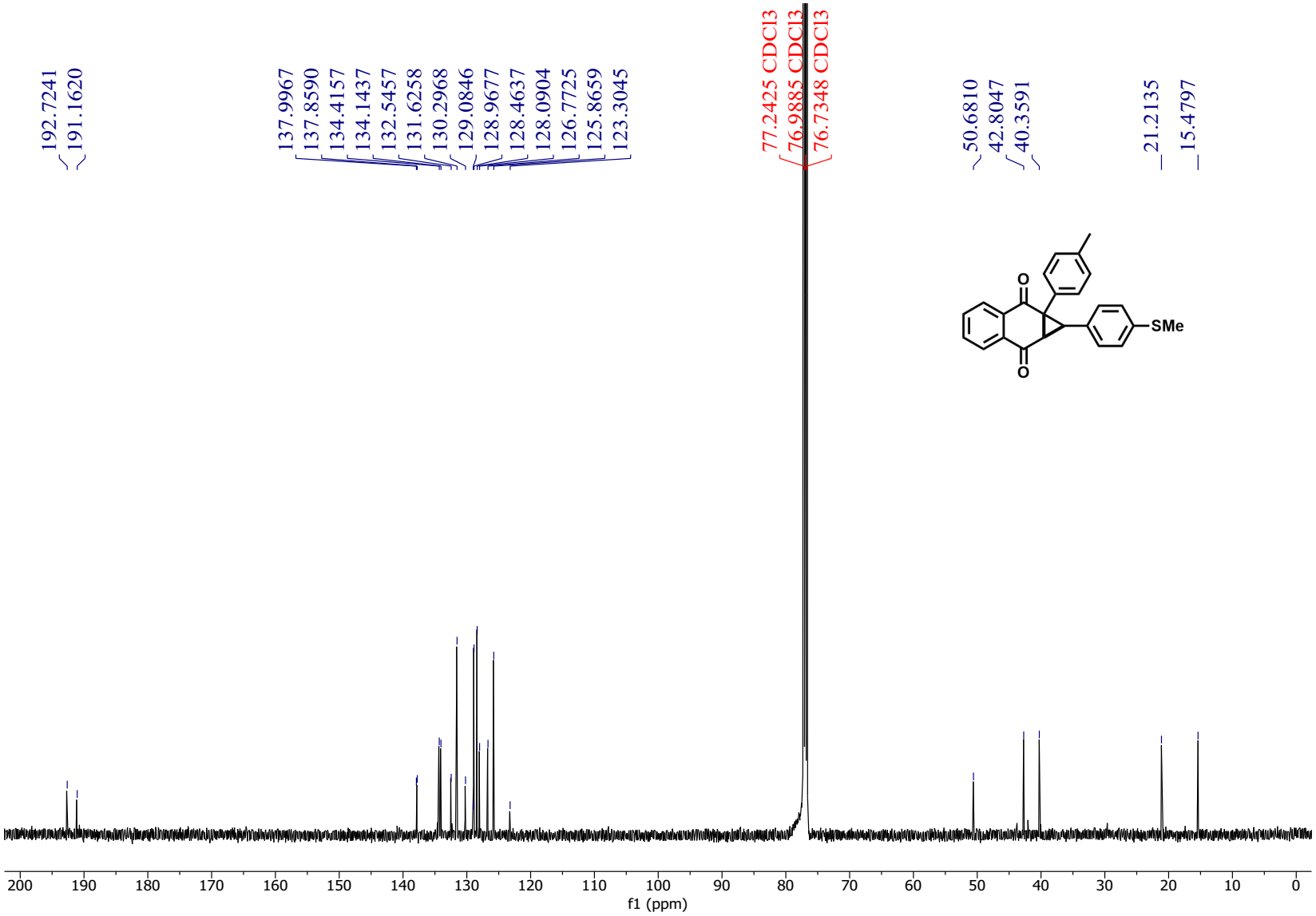
HRMS-ESI Compound **2h**



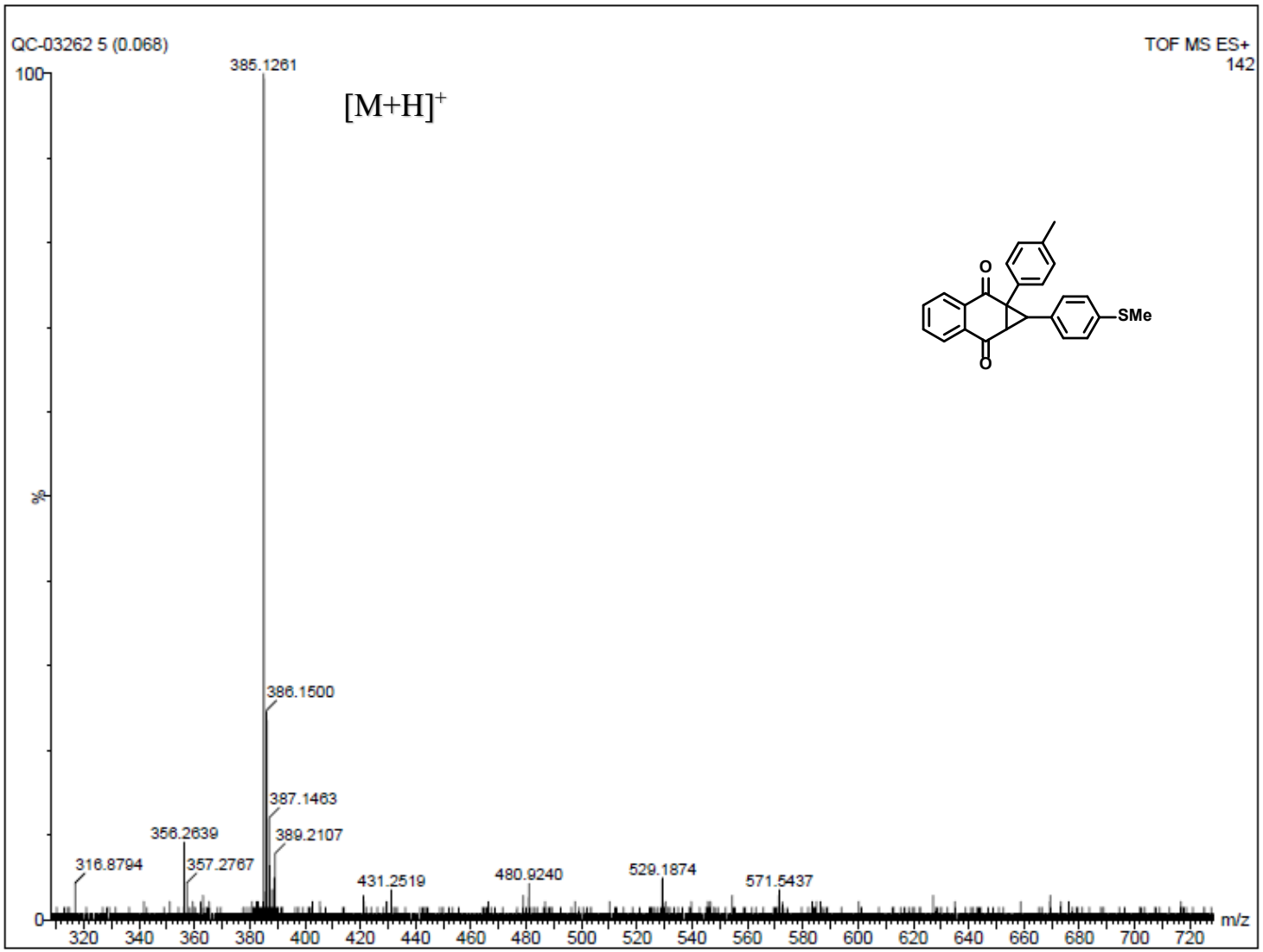
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2i**



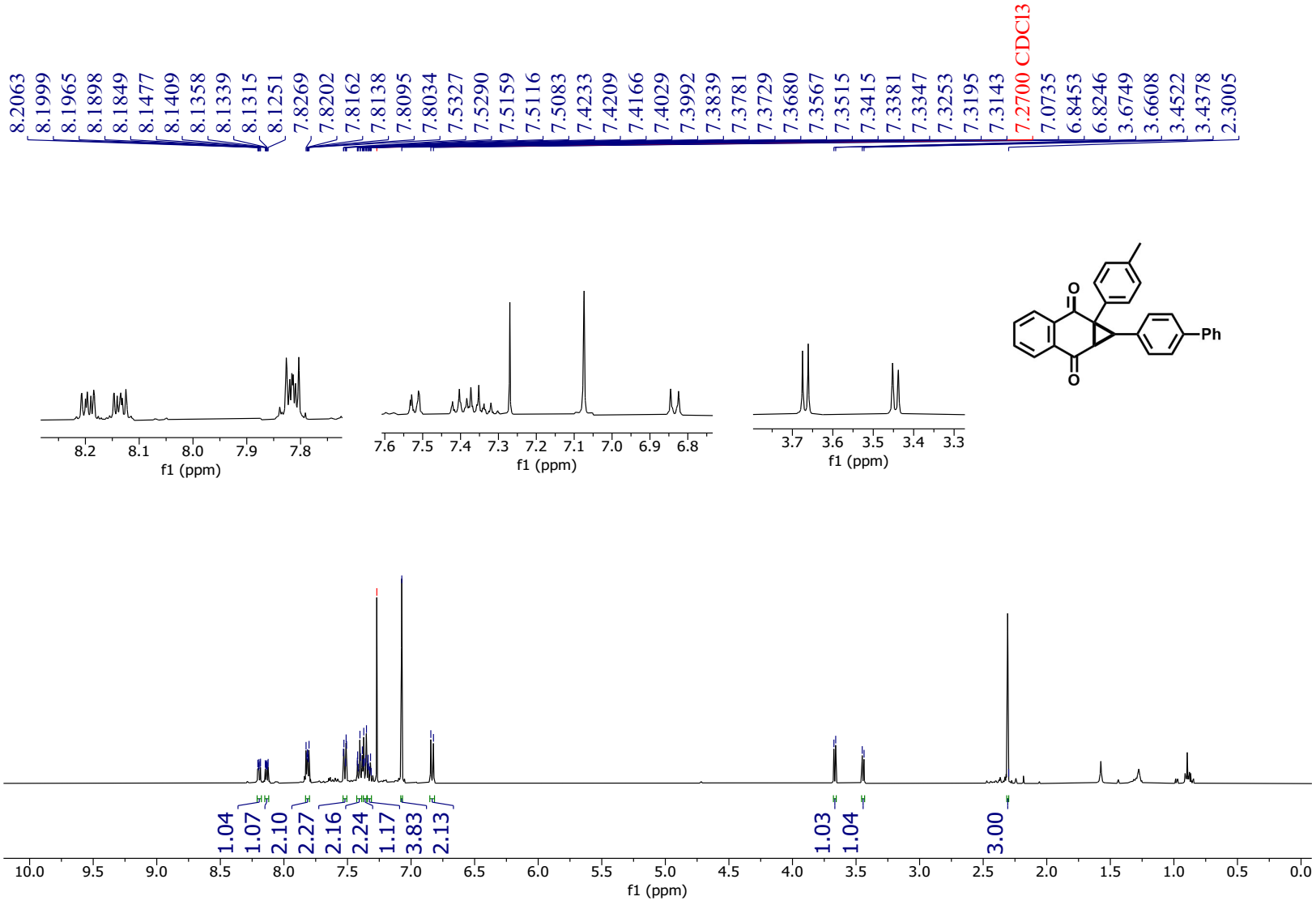
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **2i**



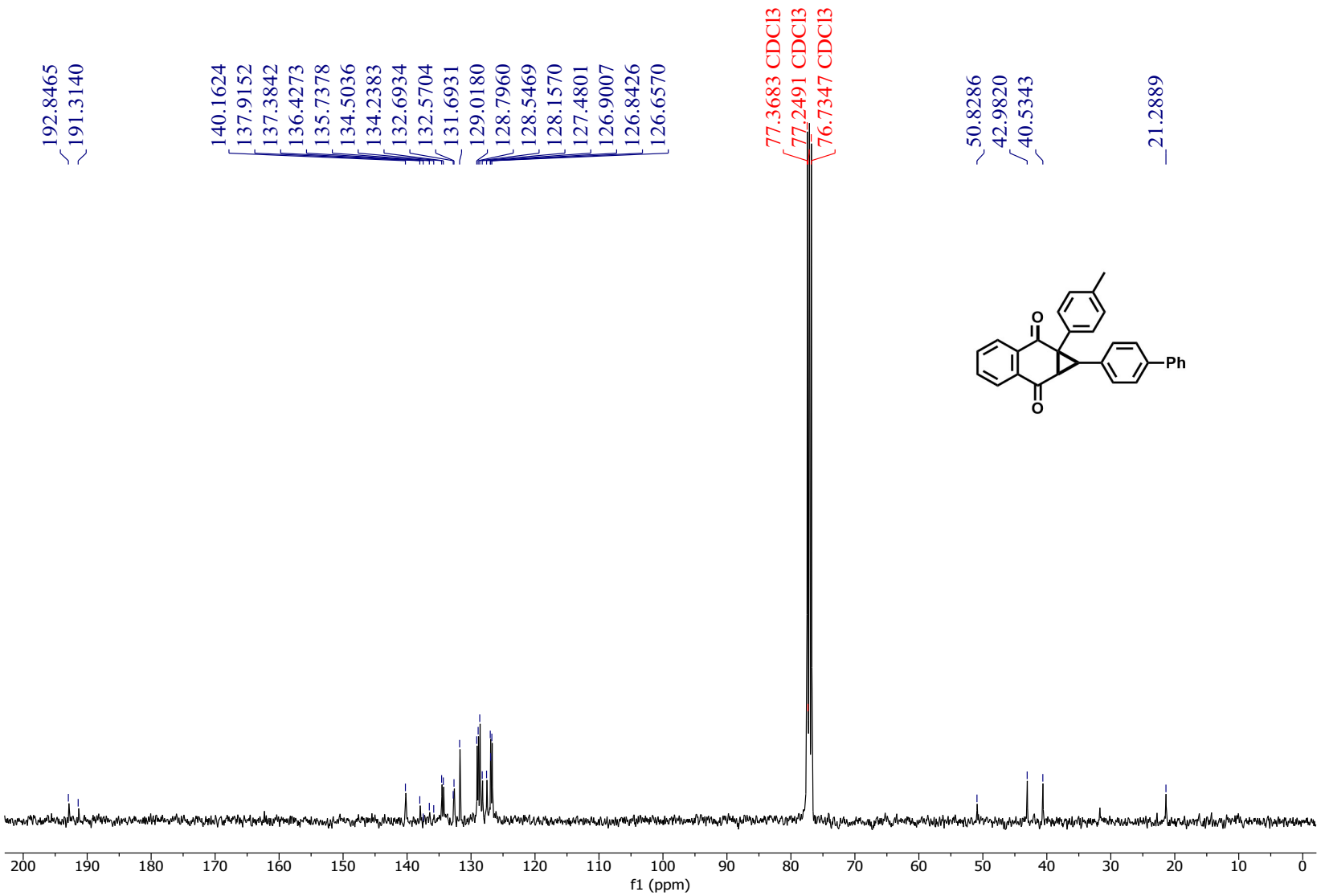
HRMS-ESI Compound **2i**



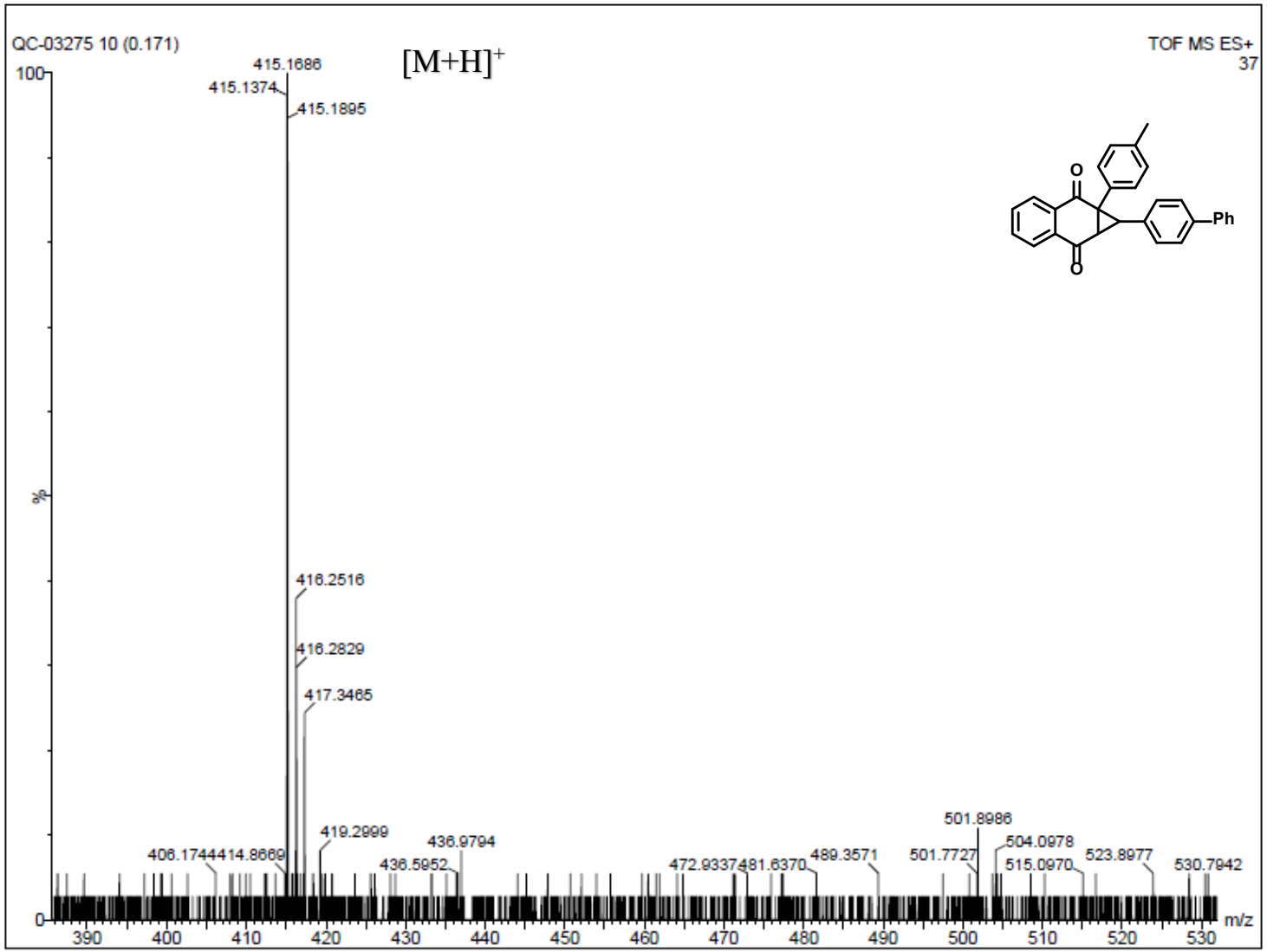
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2j**



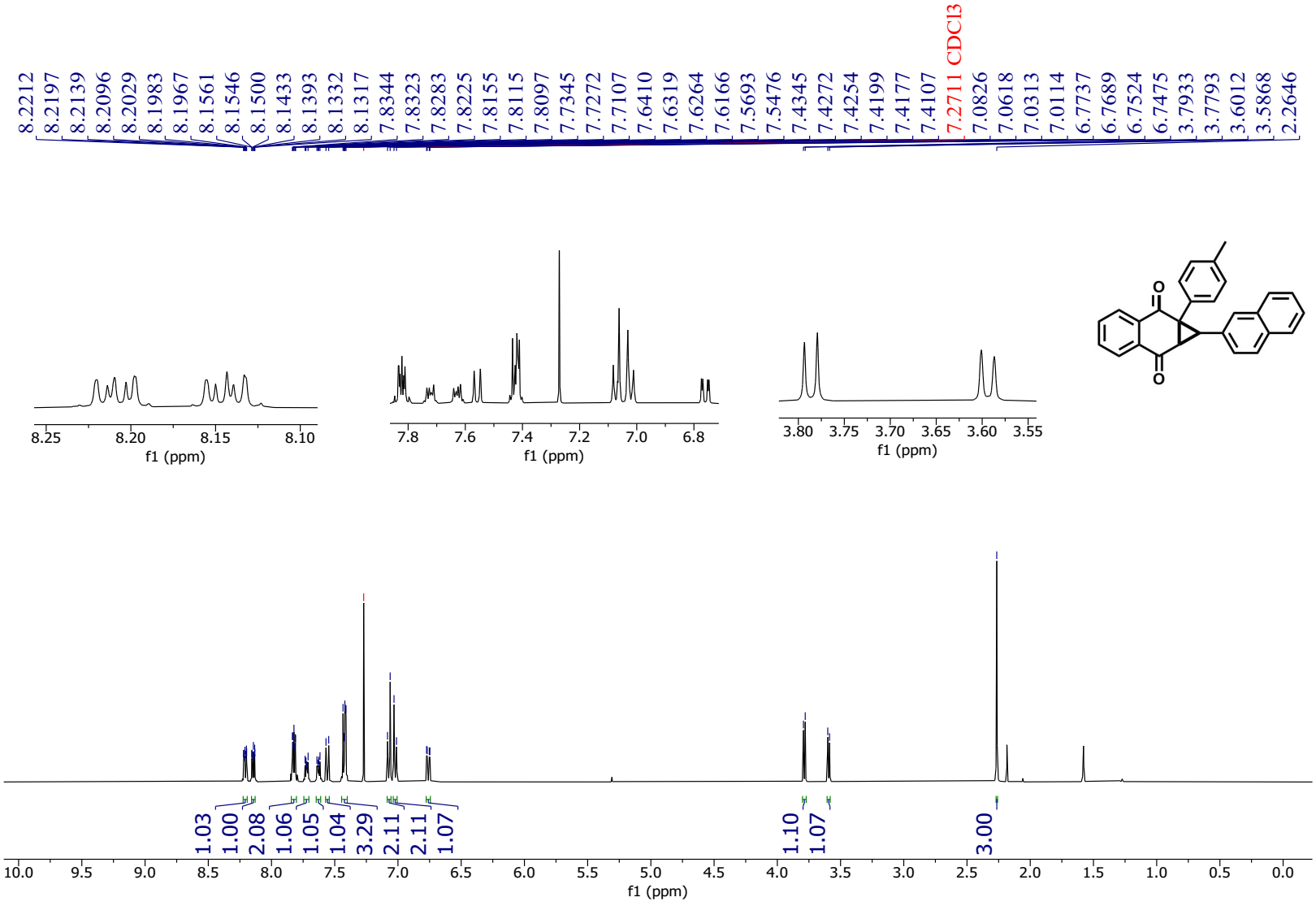
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2j**



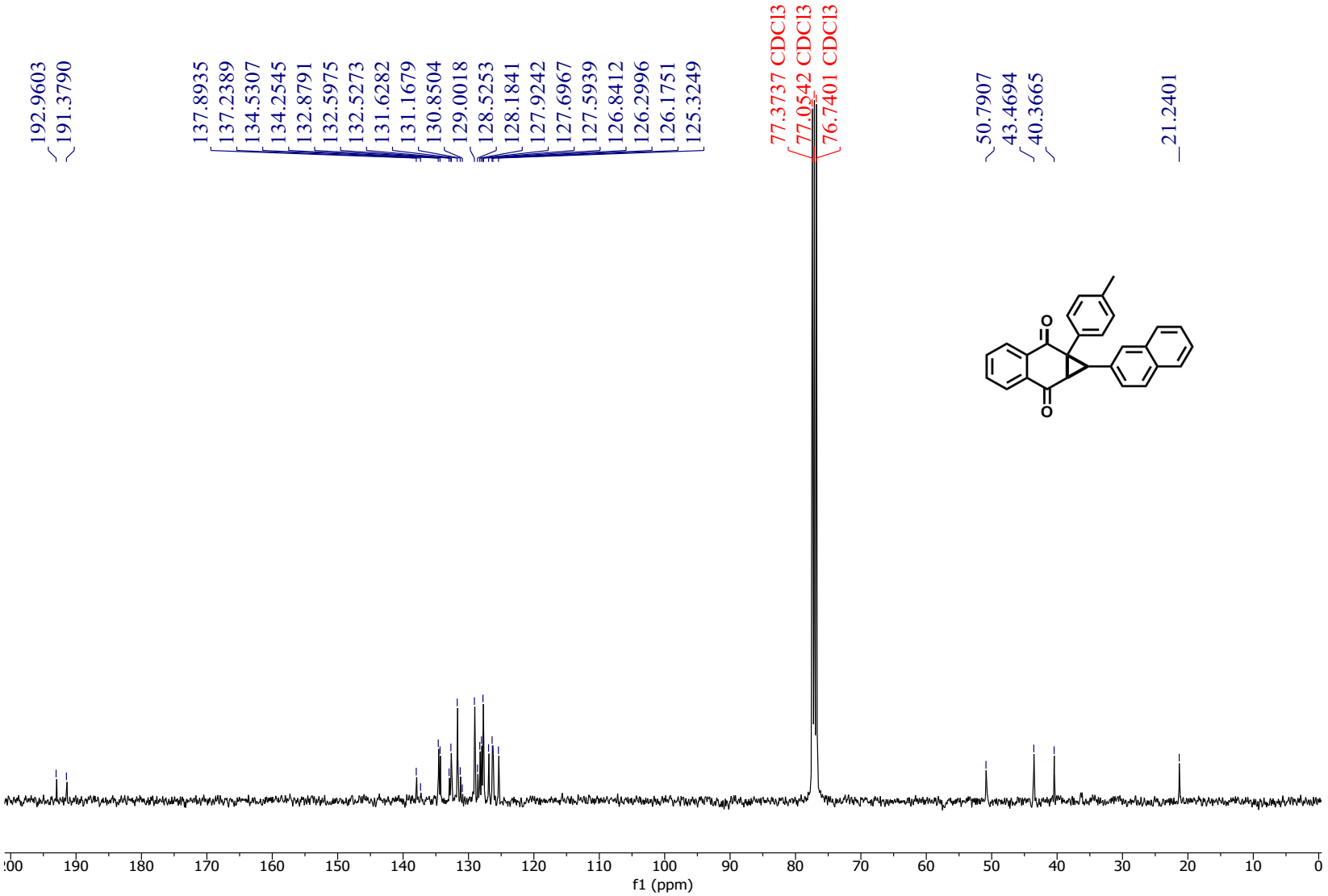
HRMS-ESI Compound **2j**



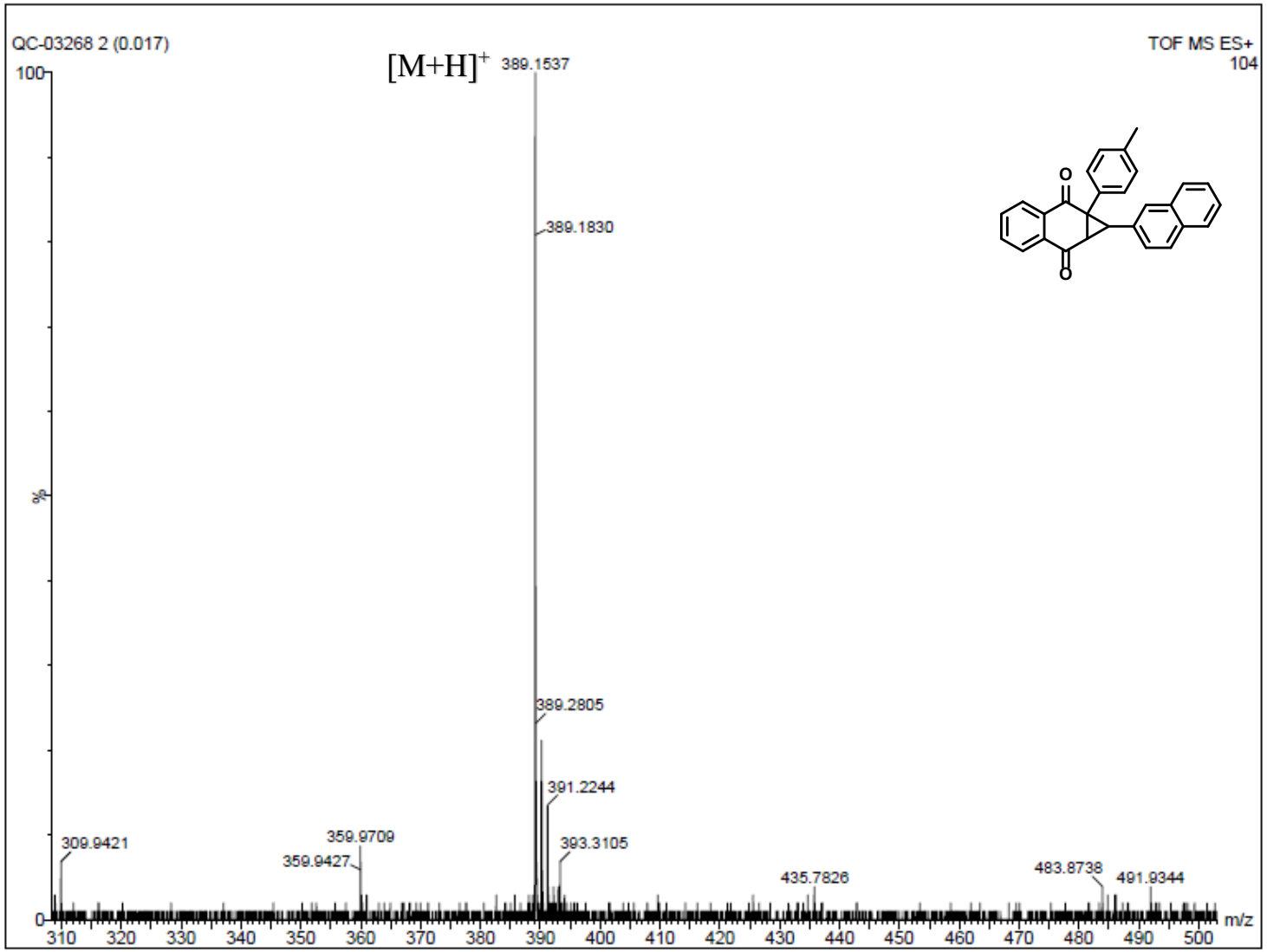
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2k**



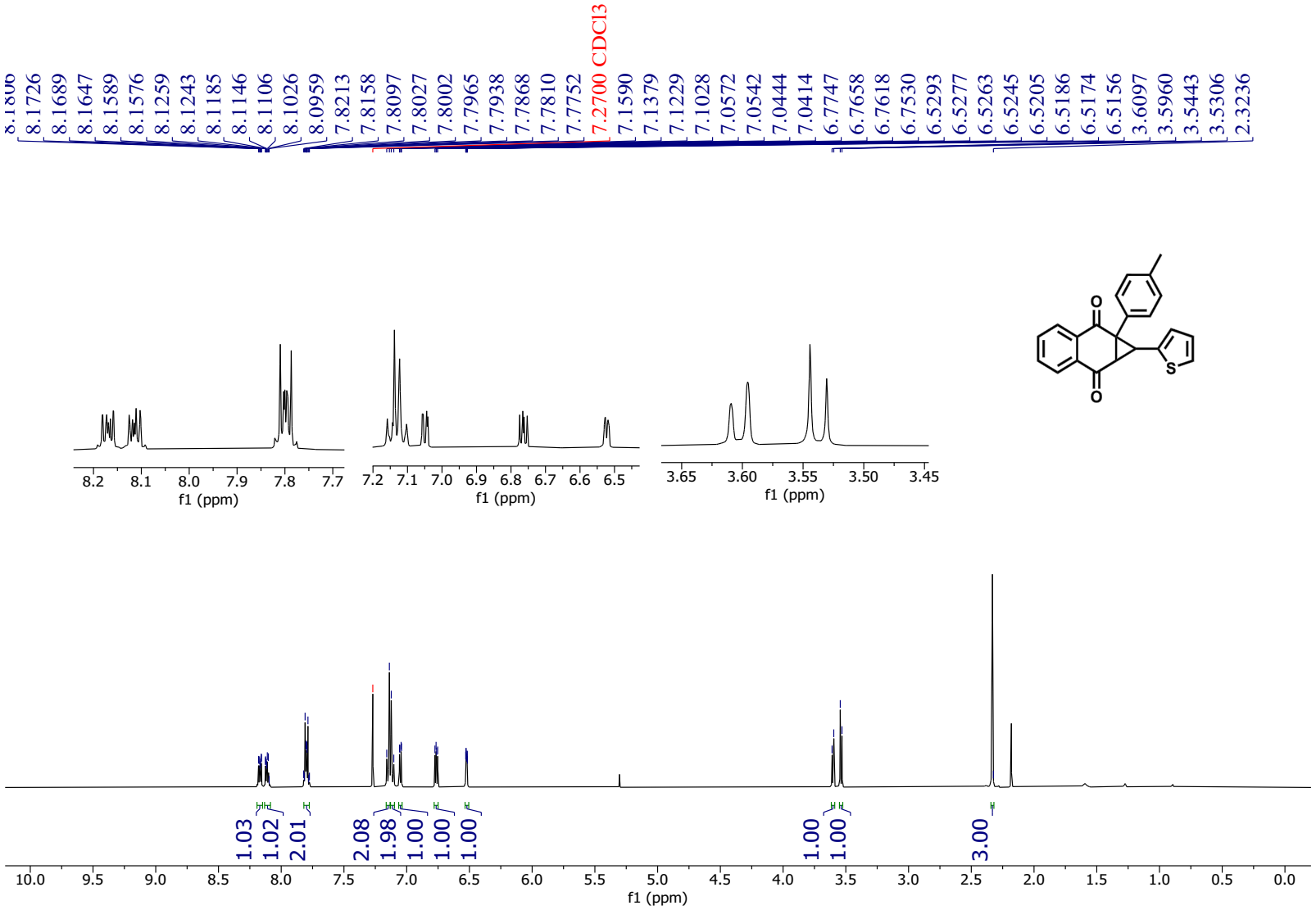
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2k**



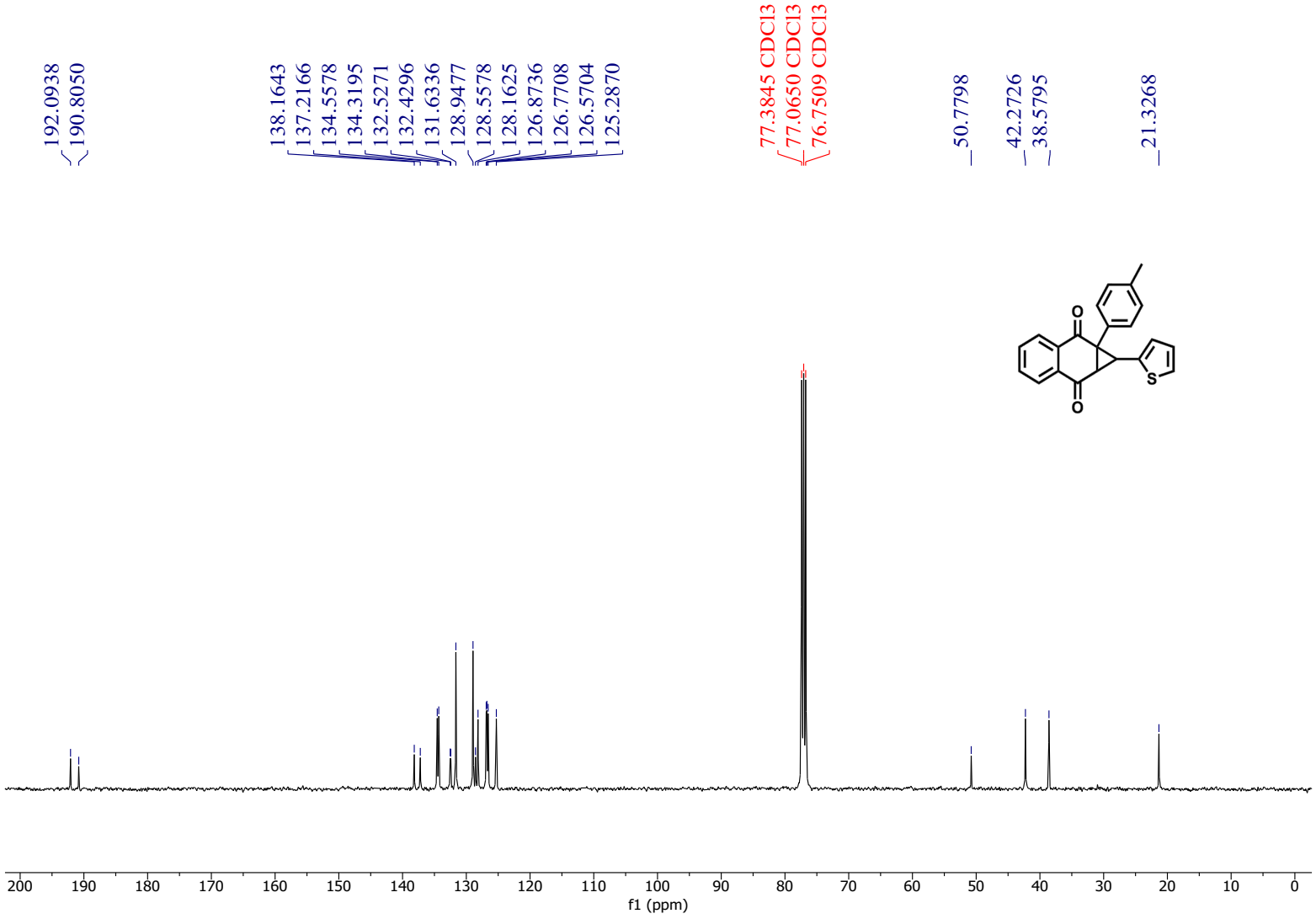
HRMS-ESI Compound **2k**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2l**



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2l**



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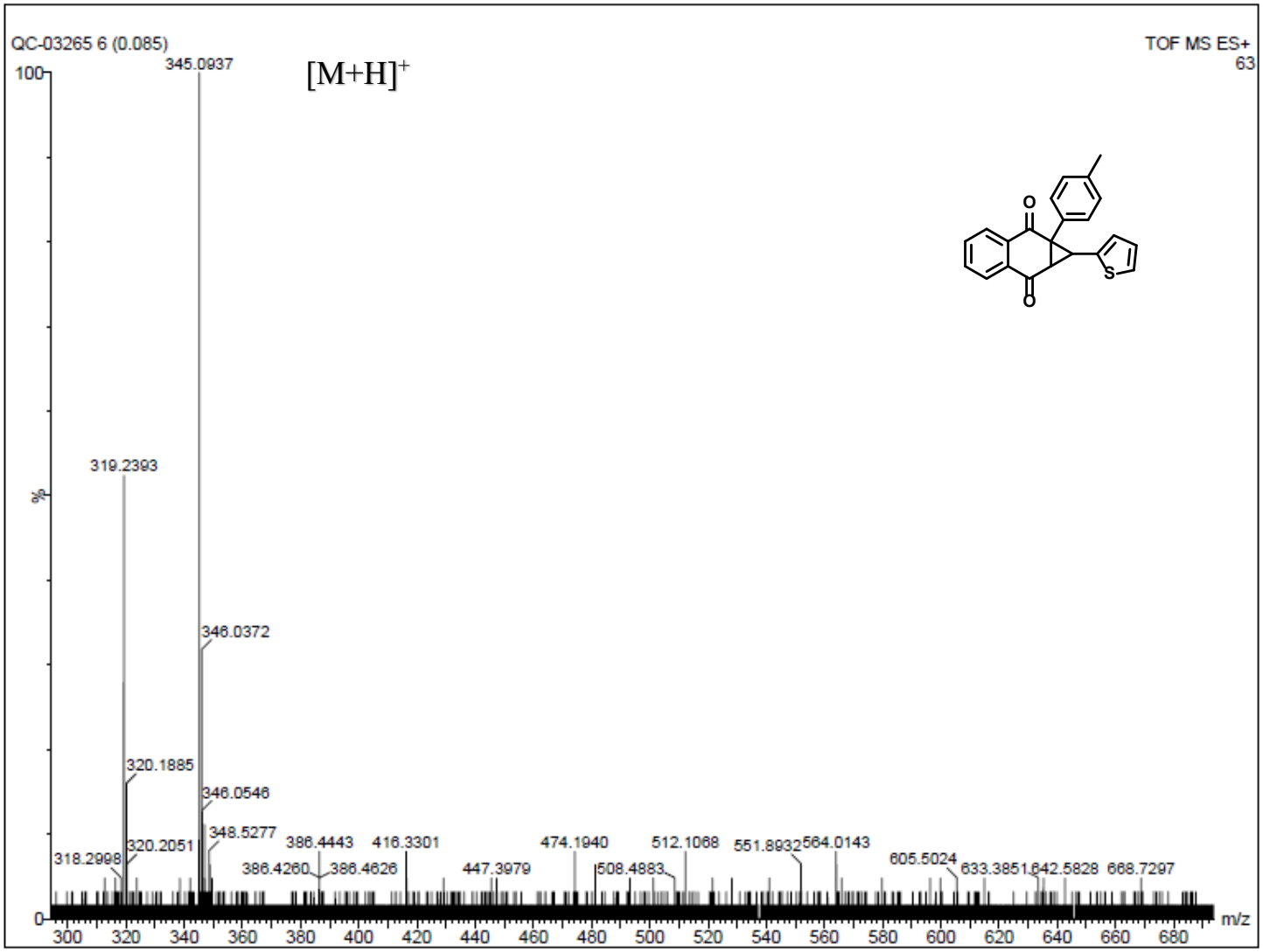
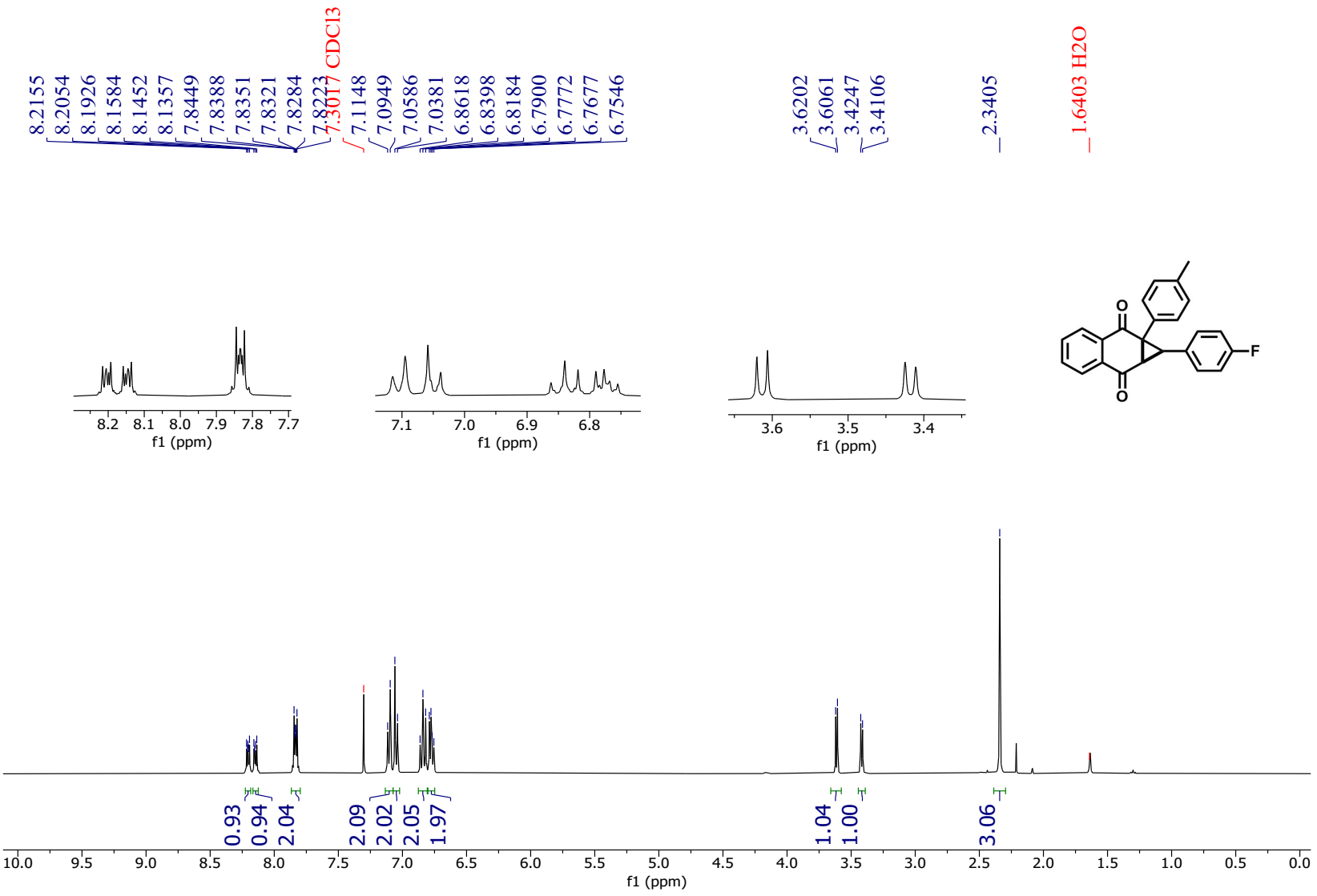
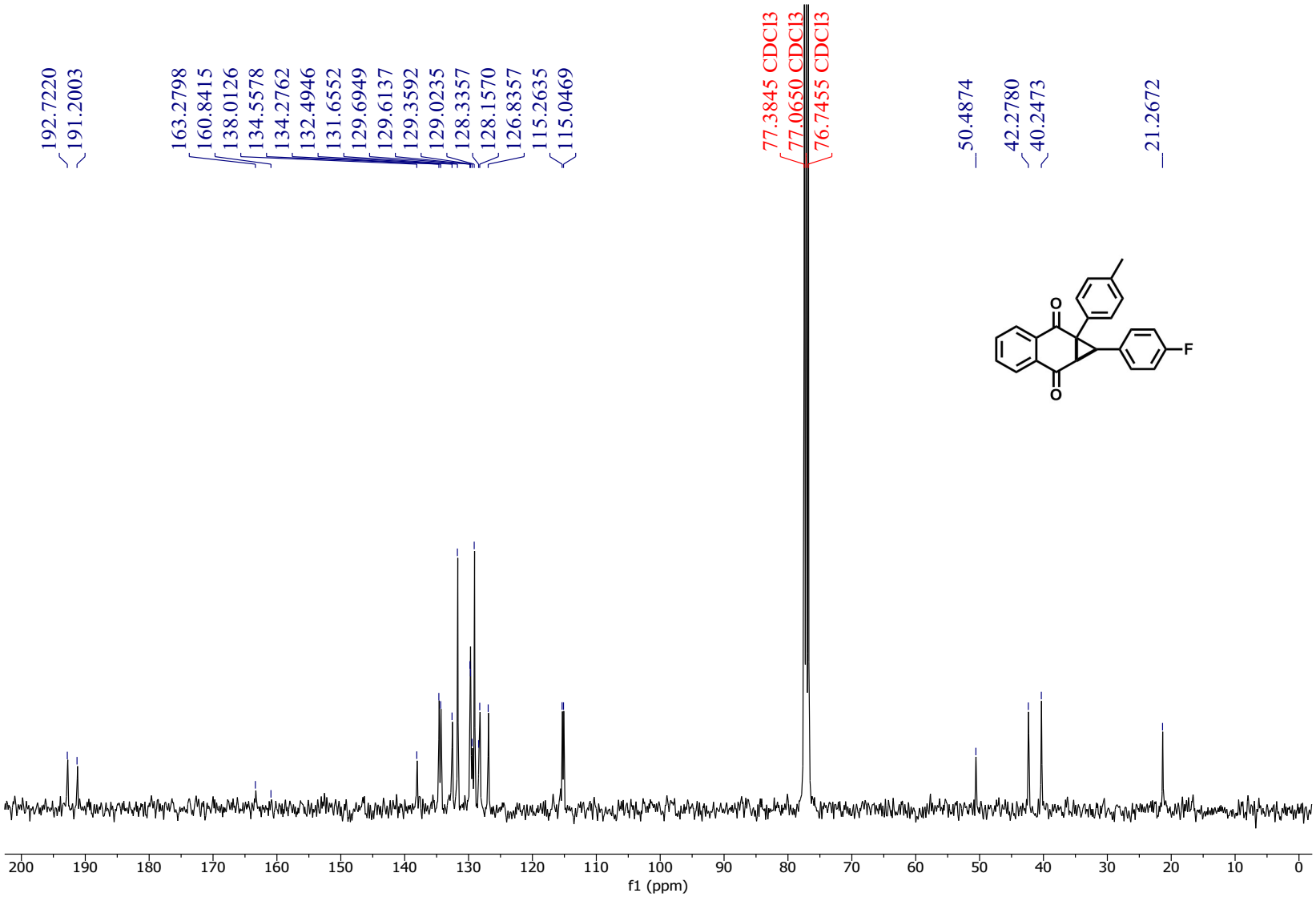


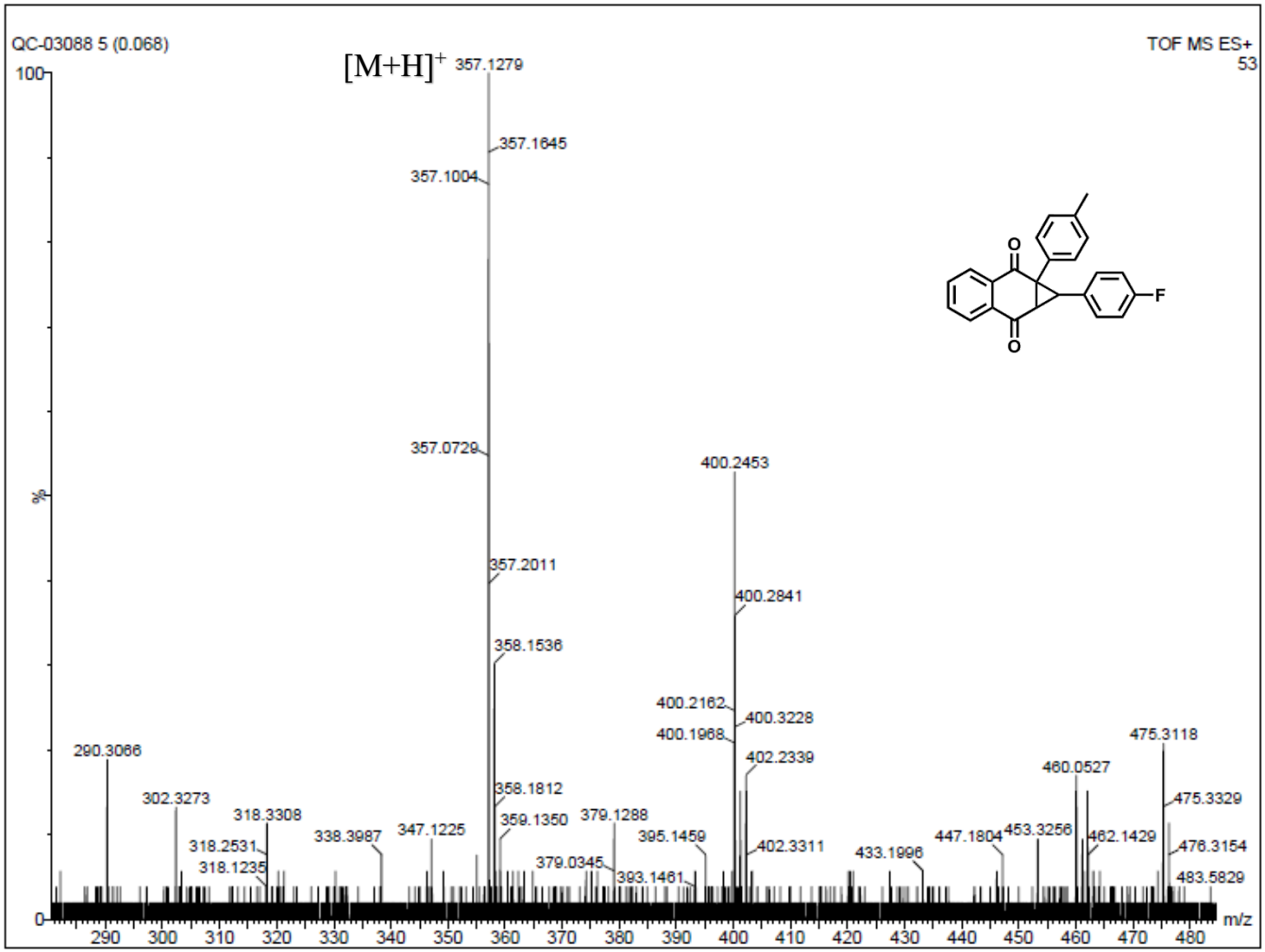
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2m**



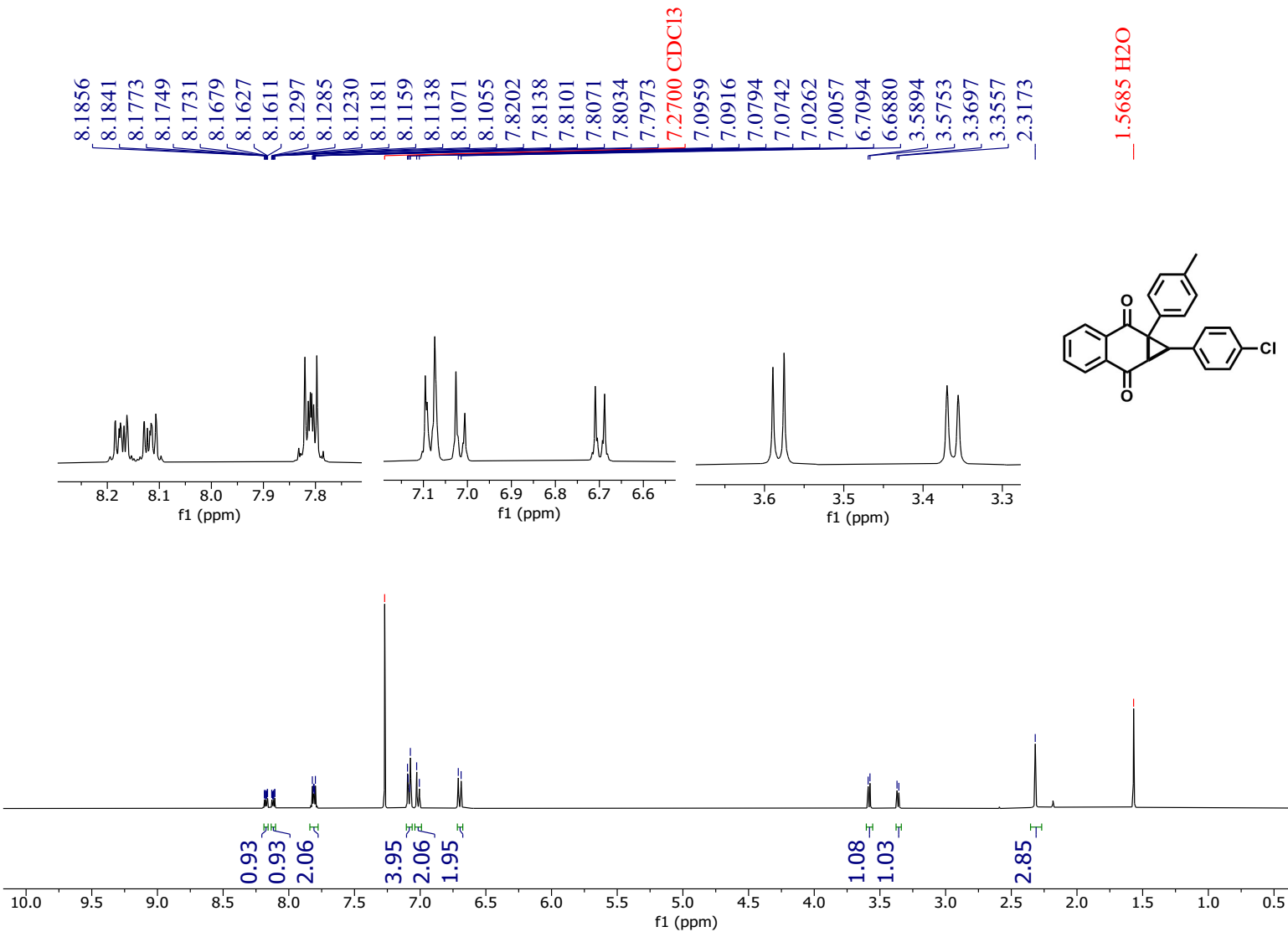
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2m**



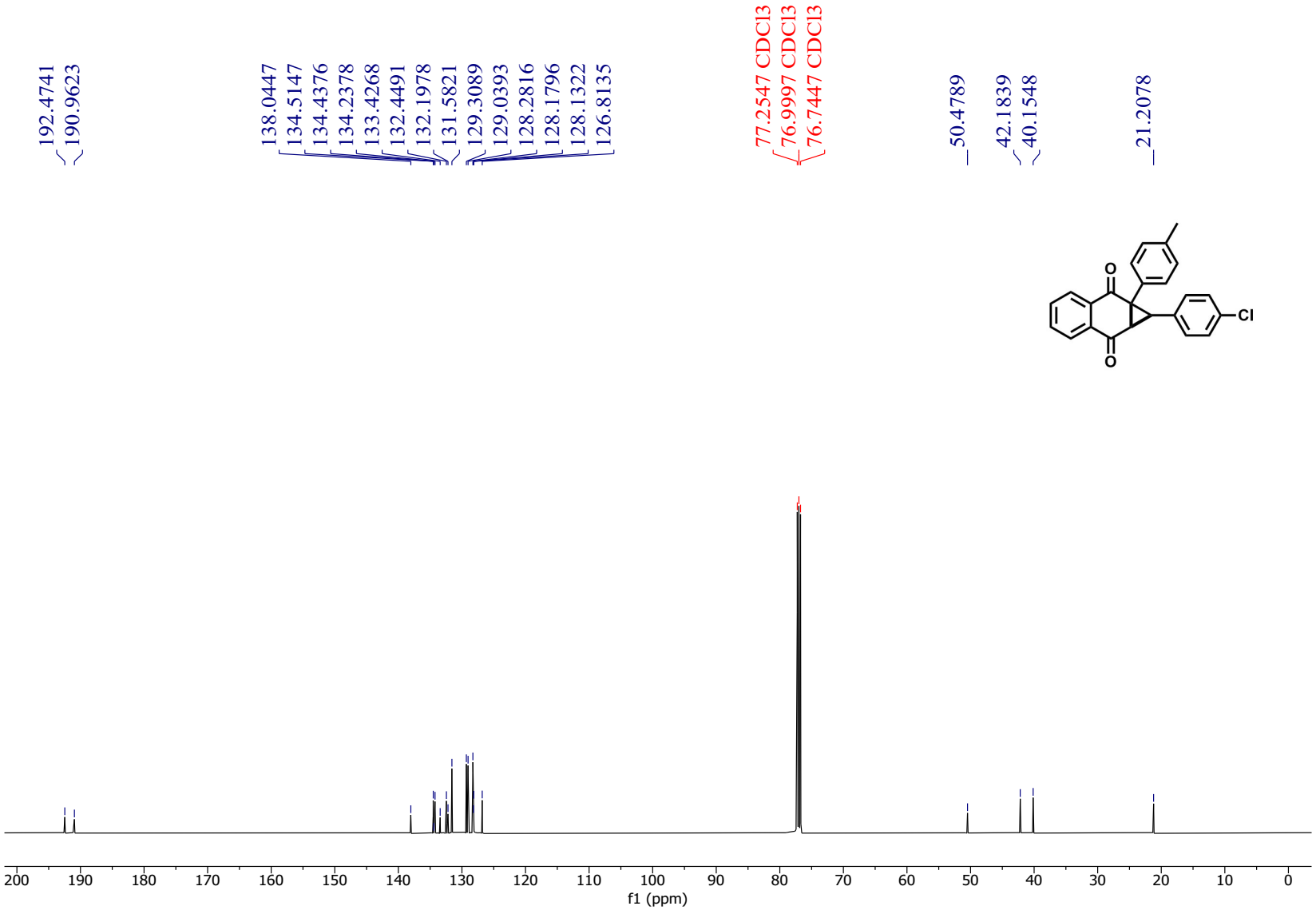
HRMS-ESI Compound **2m**



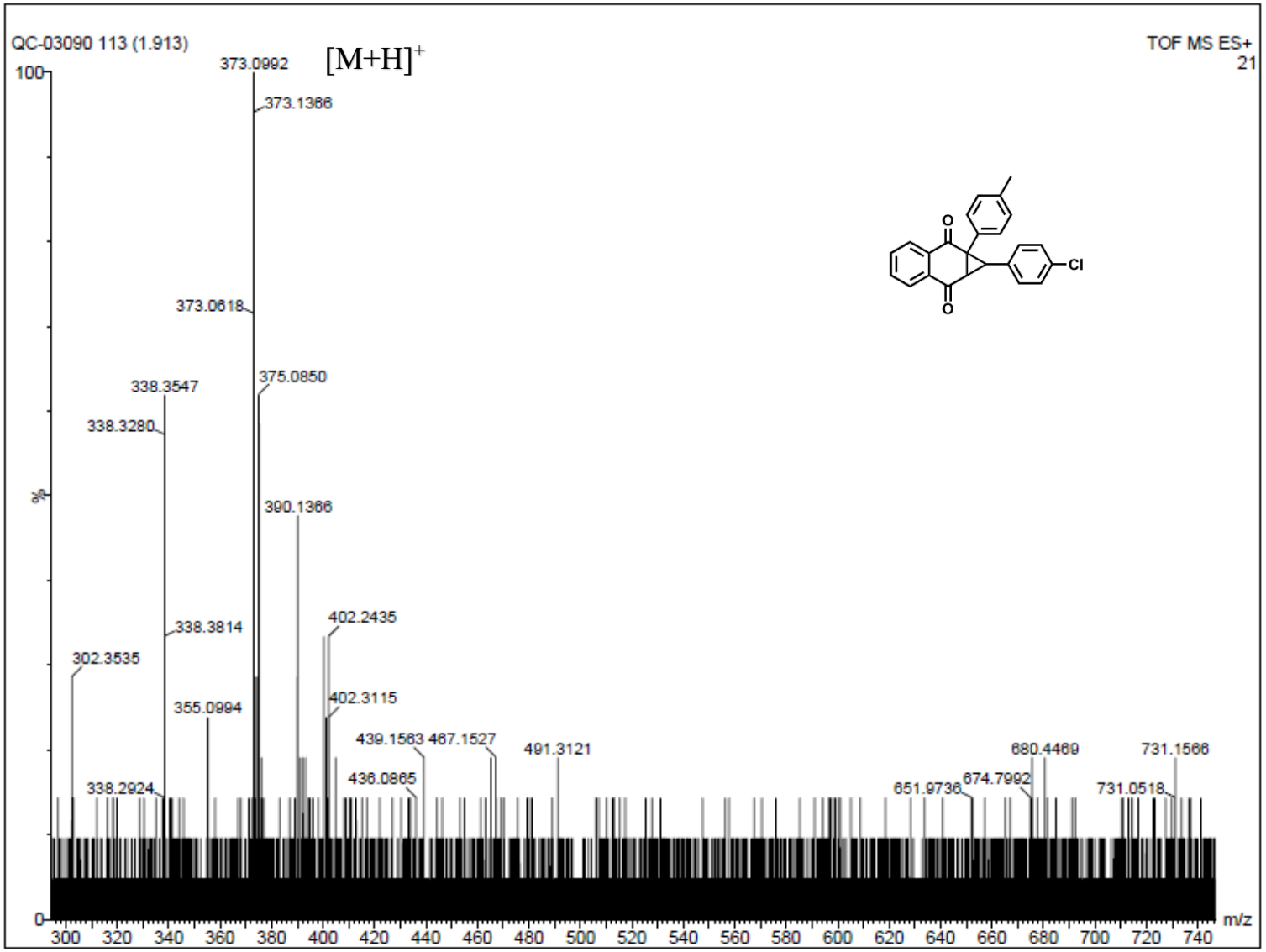
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2n**



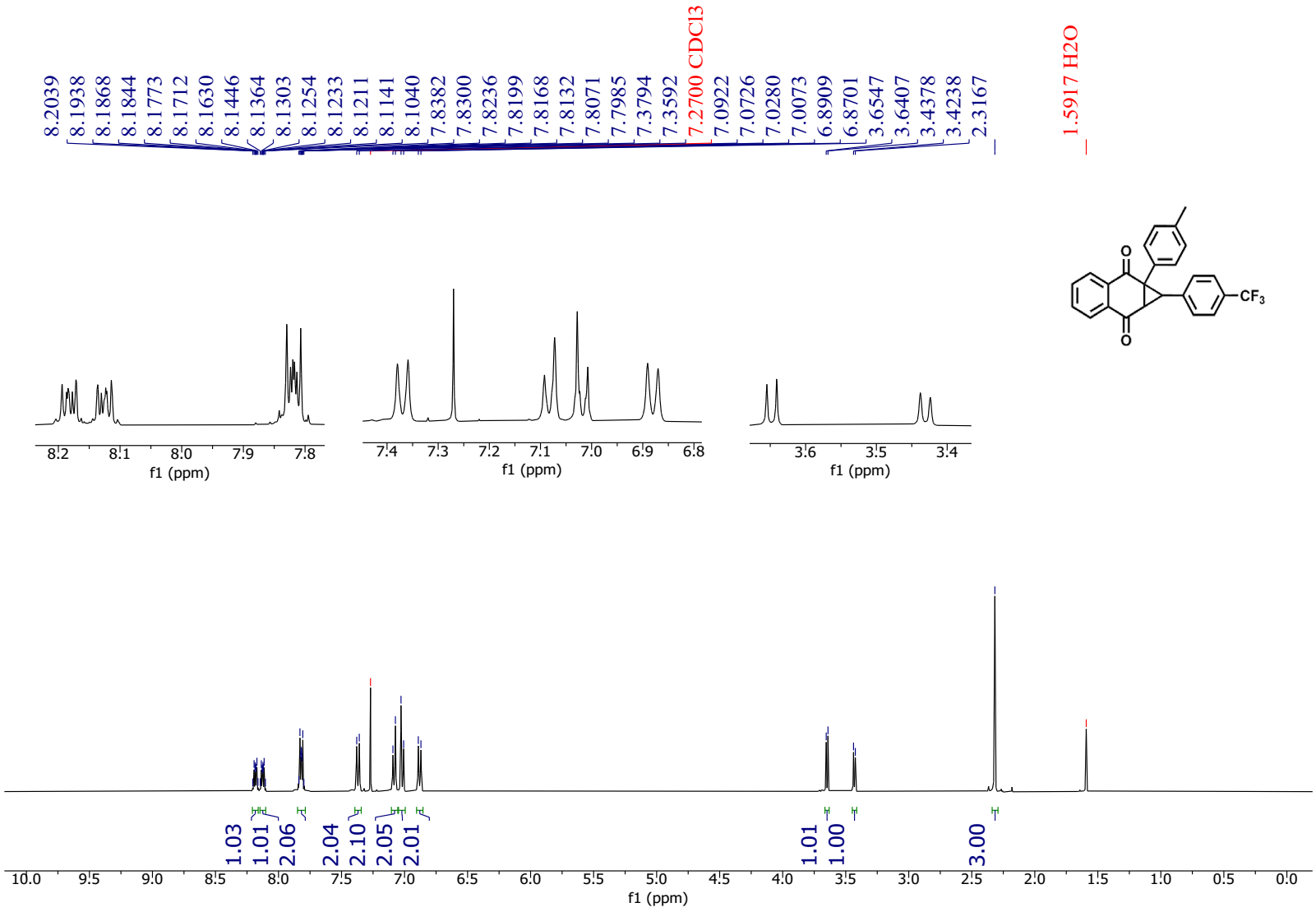
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **2n**



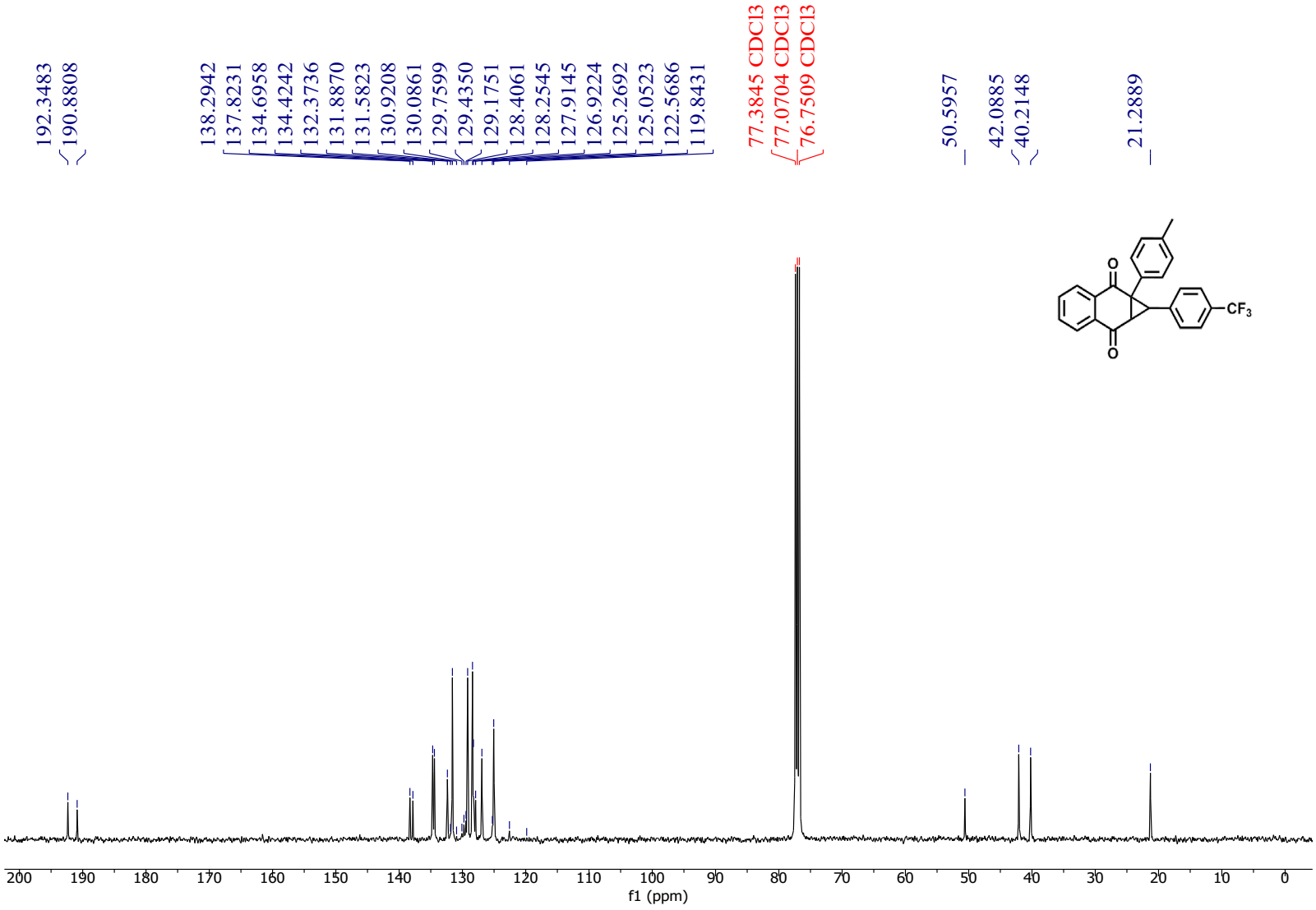
HRMS-ESI Compound **2n**



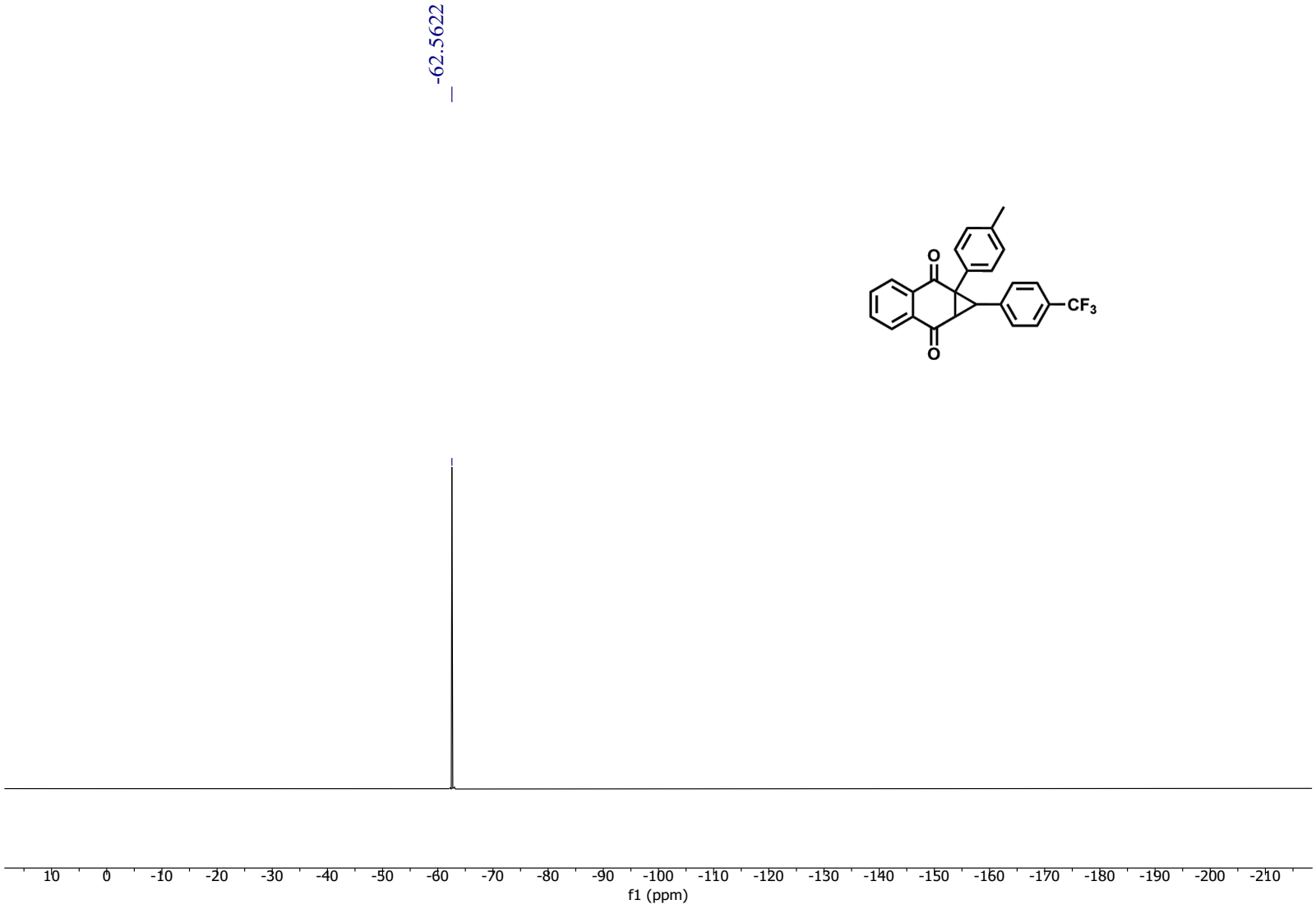
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2o**



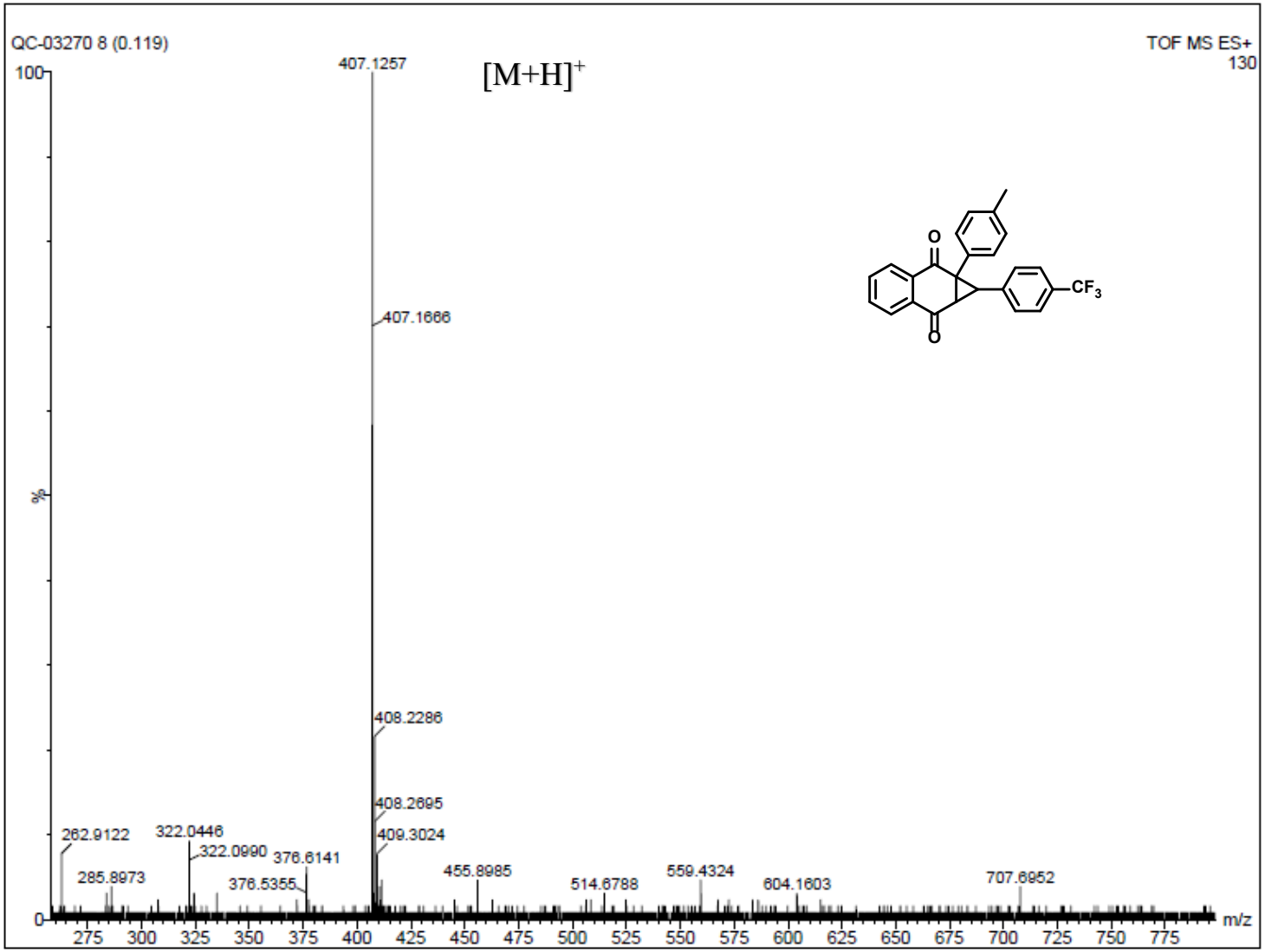
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2o**



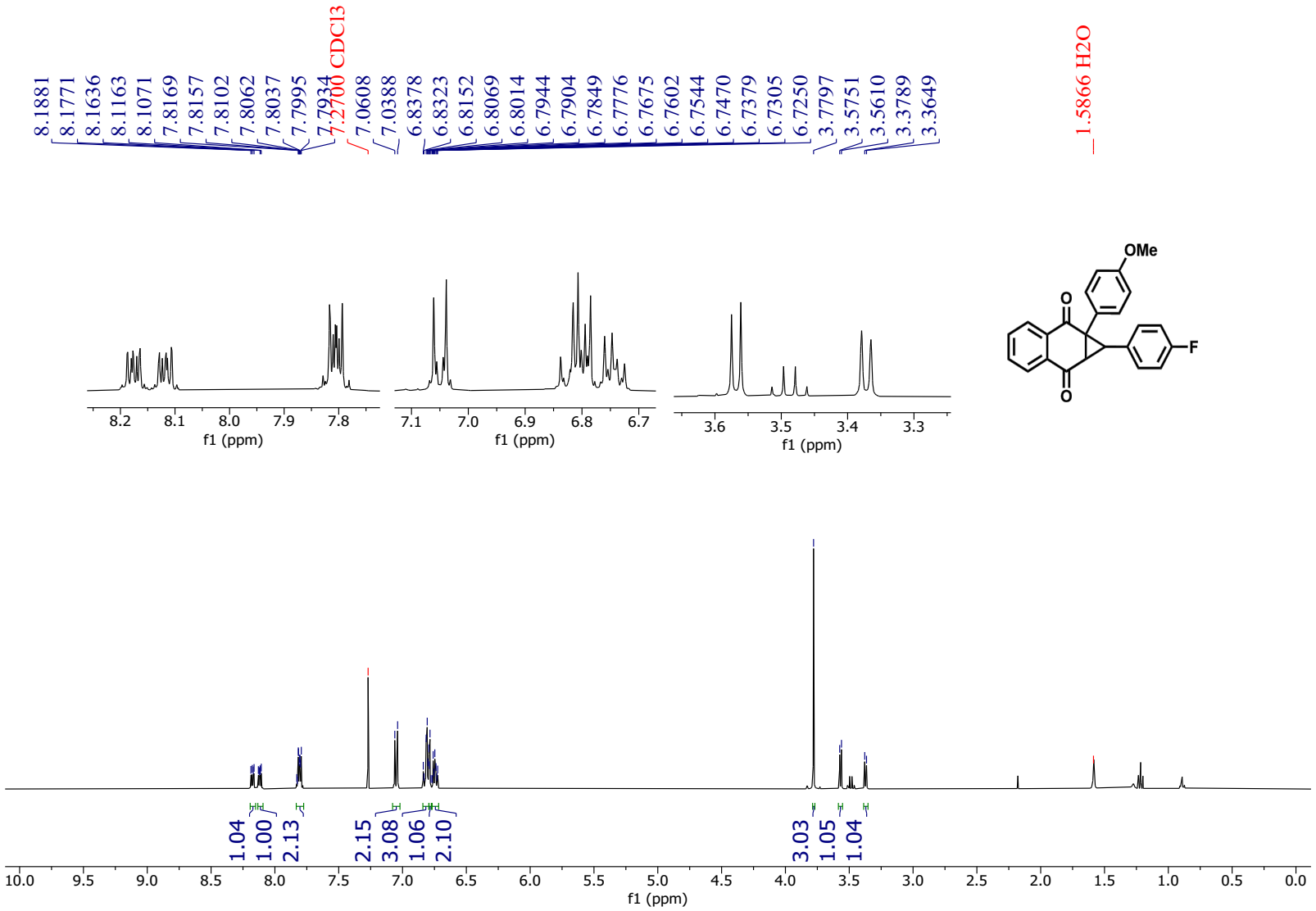
^{19}F NMR (377 MHz, $CDCl_3$) spectrum of **2o**



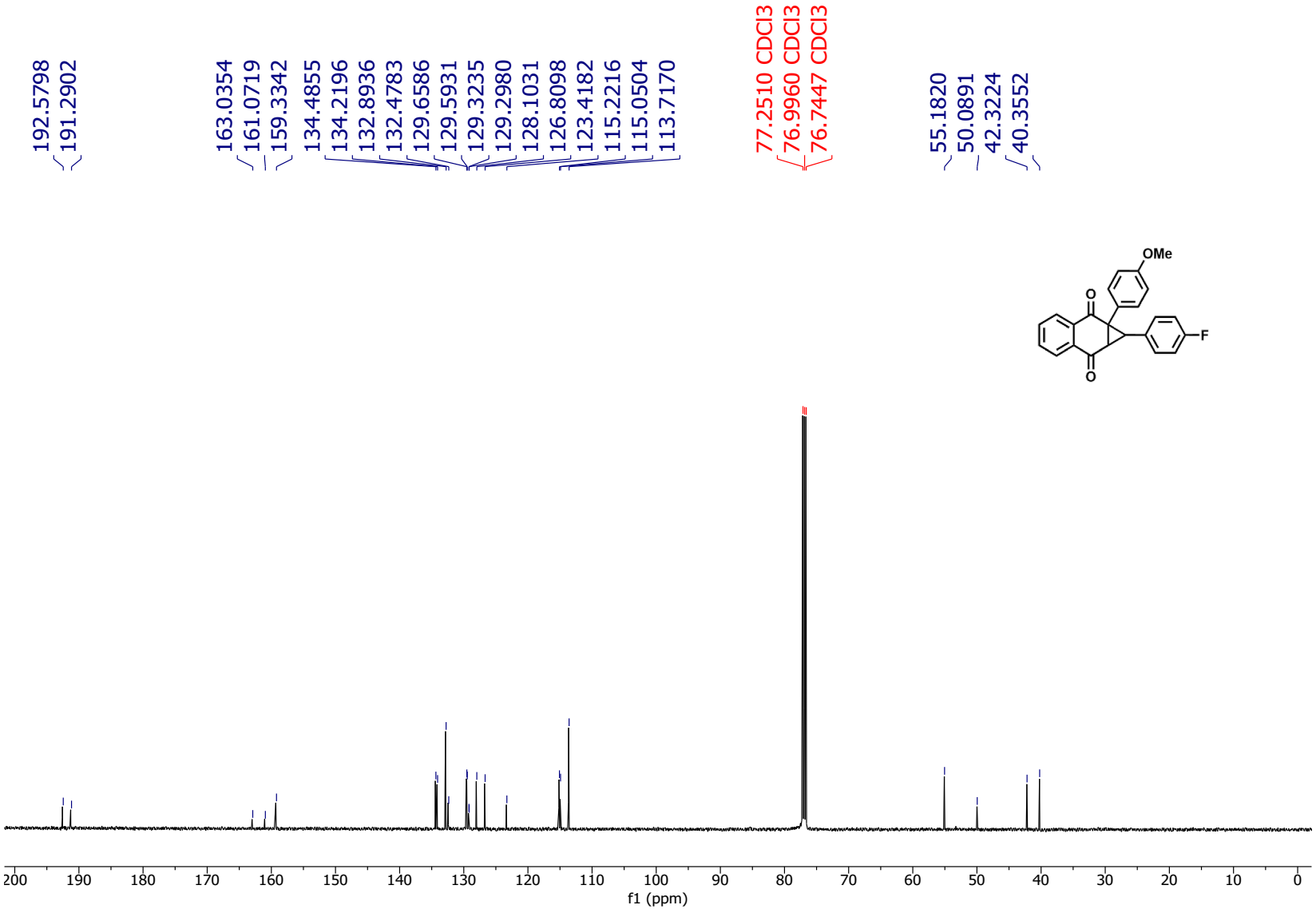
HRMS-ESI Compound **2o**



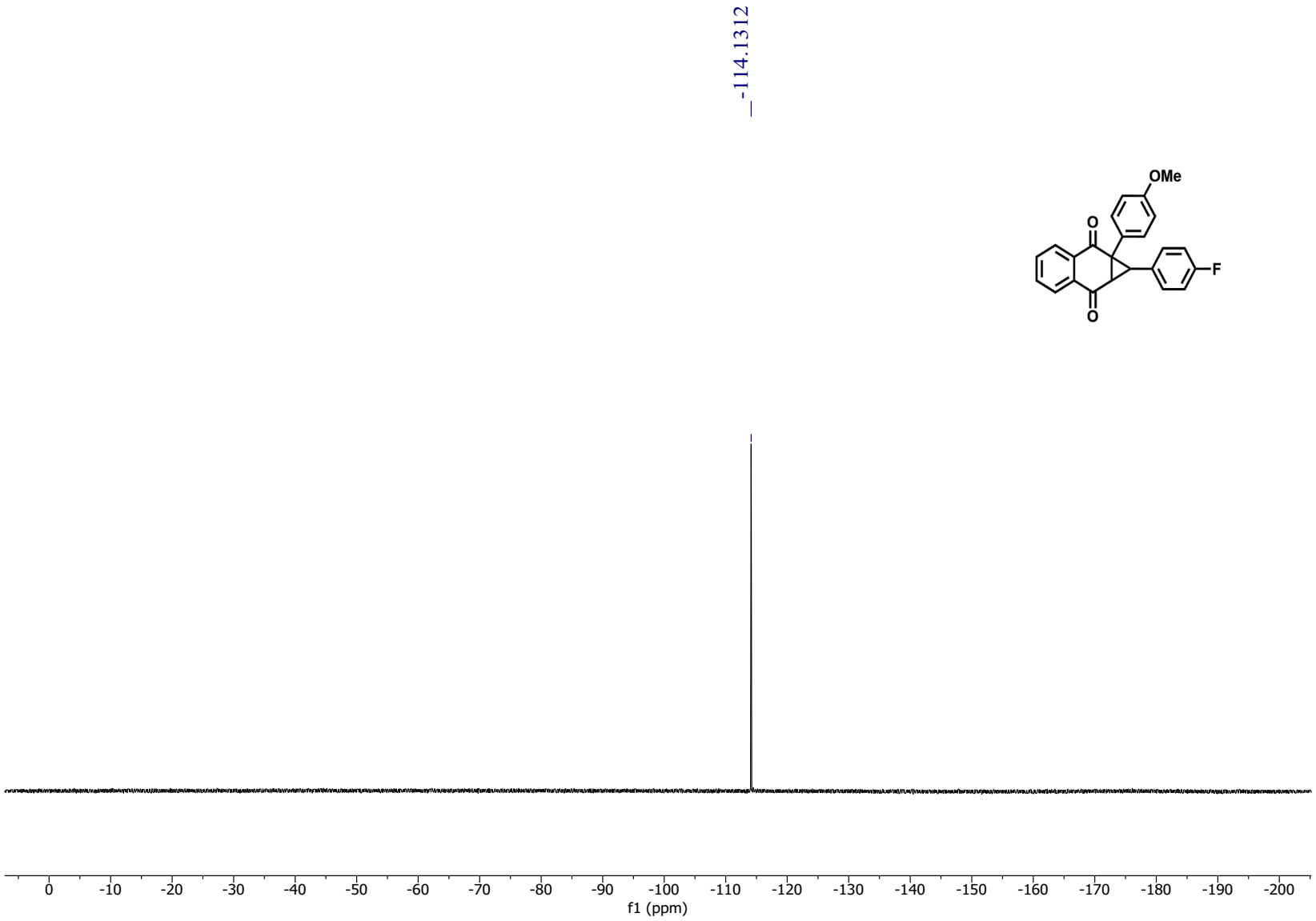
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2p**



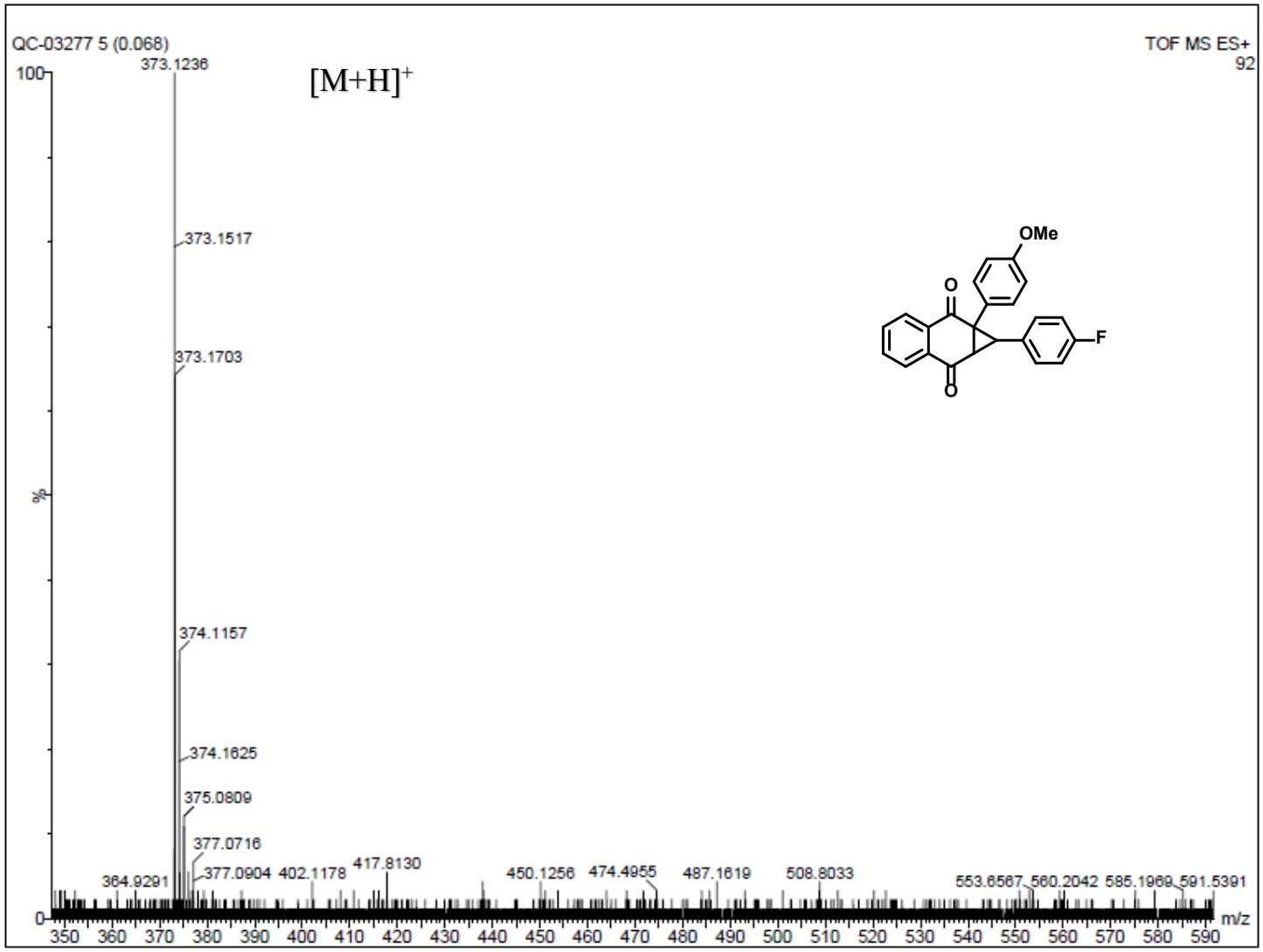
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **2p**



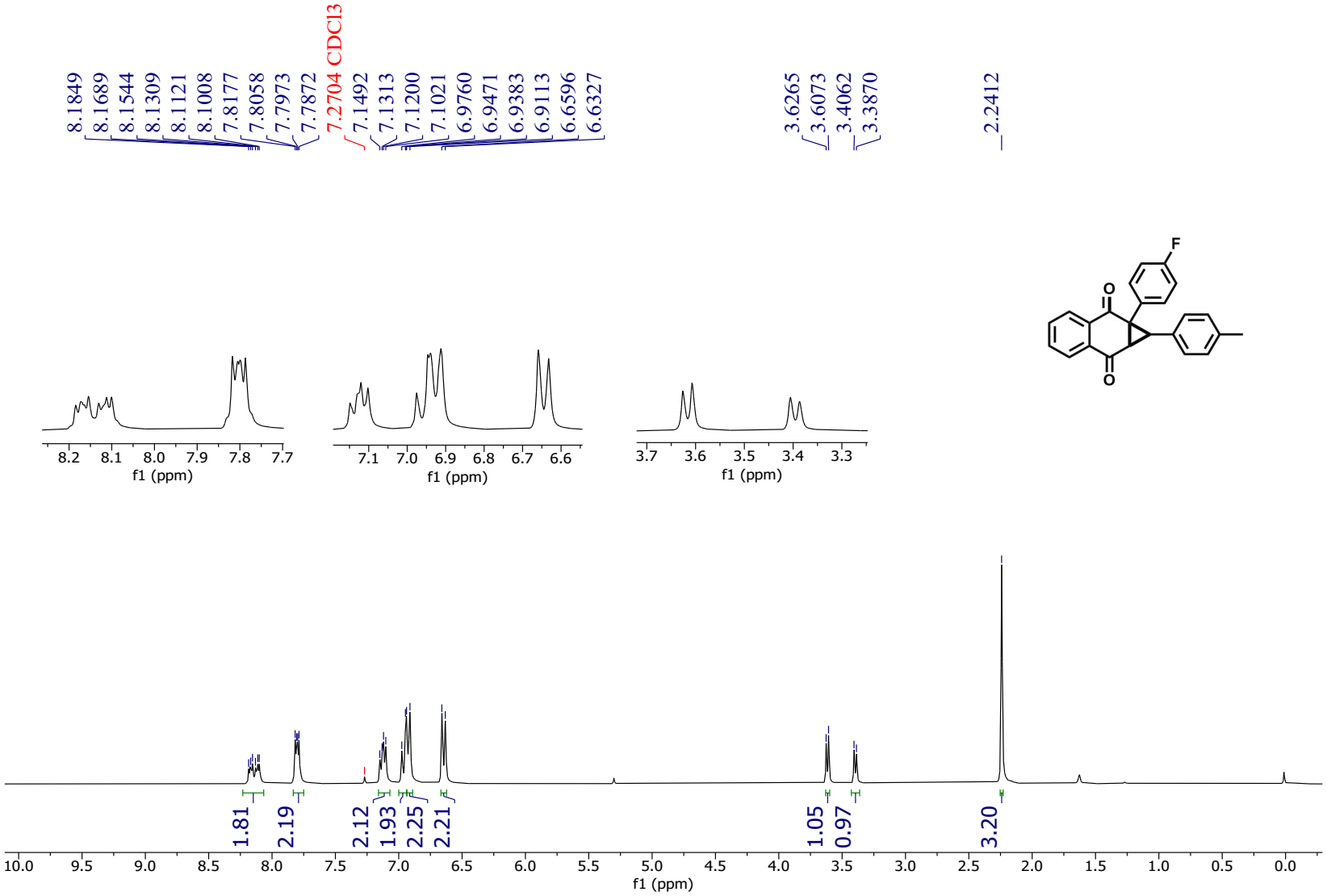
^{19}F NMR (470 MHz, $CDCl_3$) spectrum of **2p**



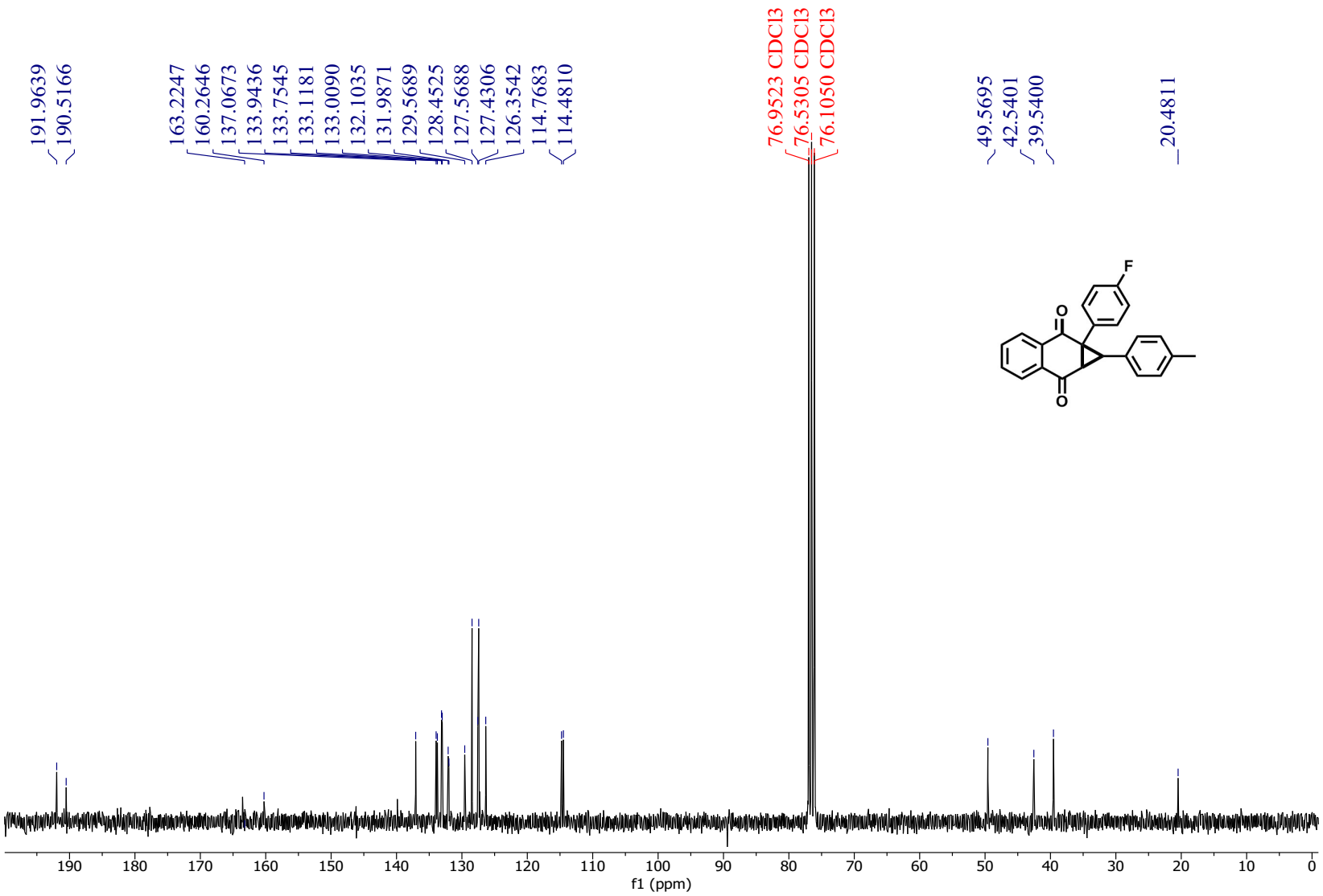
HRMS-ESI Compound **2p**



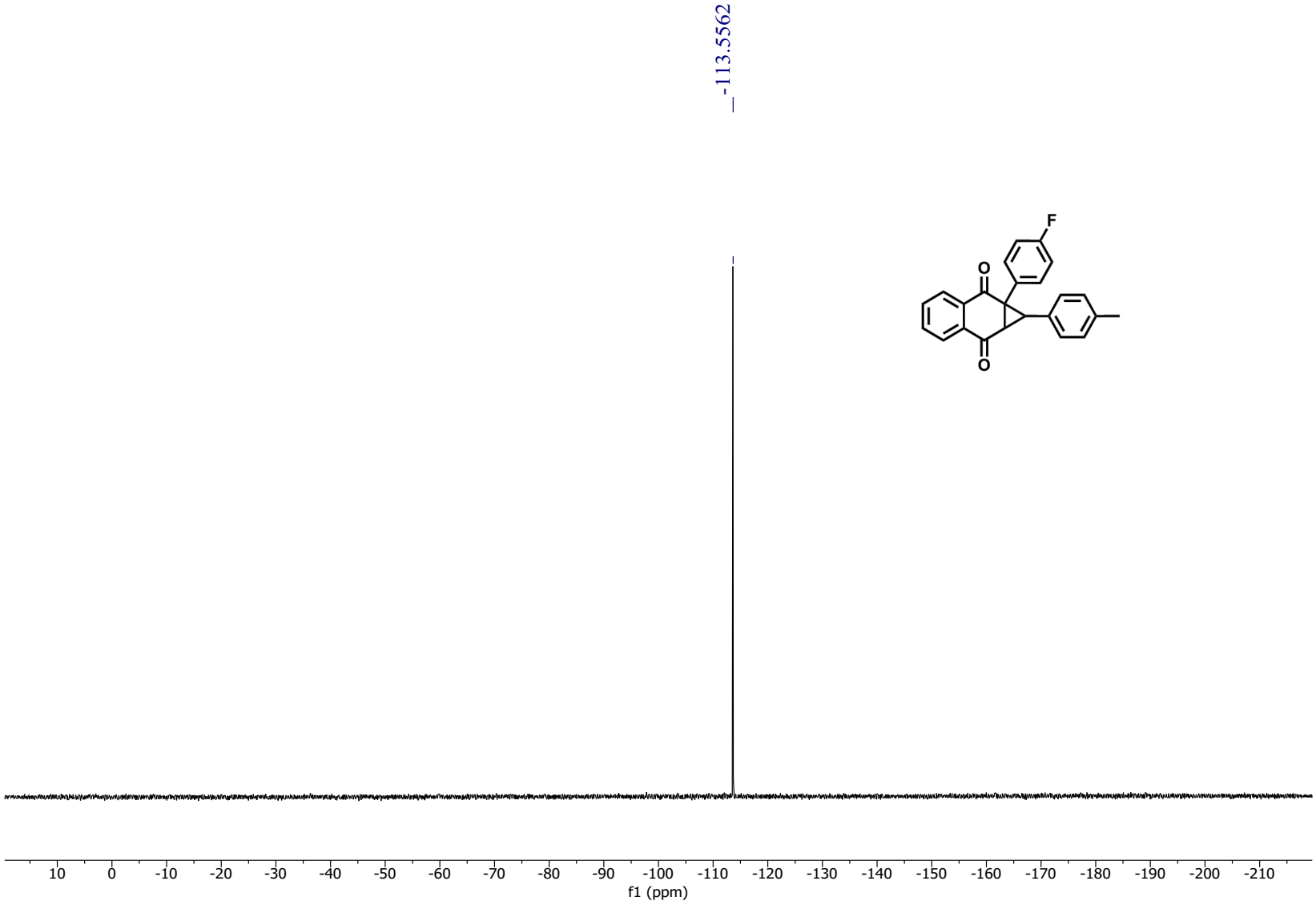
^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **2q**



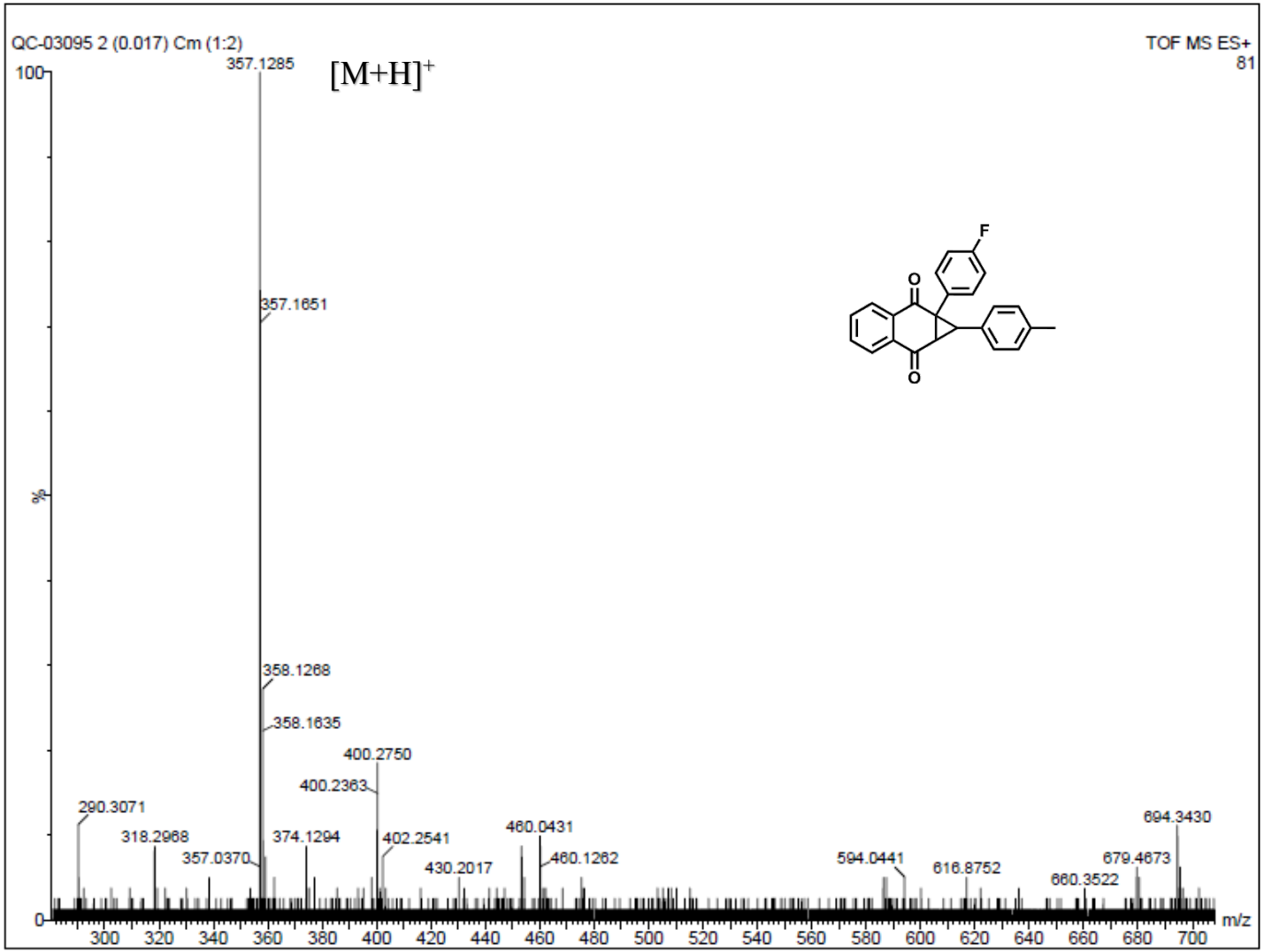
^{13}C NMR (75 MHz, $CDCl_3$) spectrum of **2q**



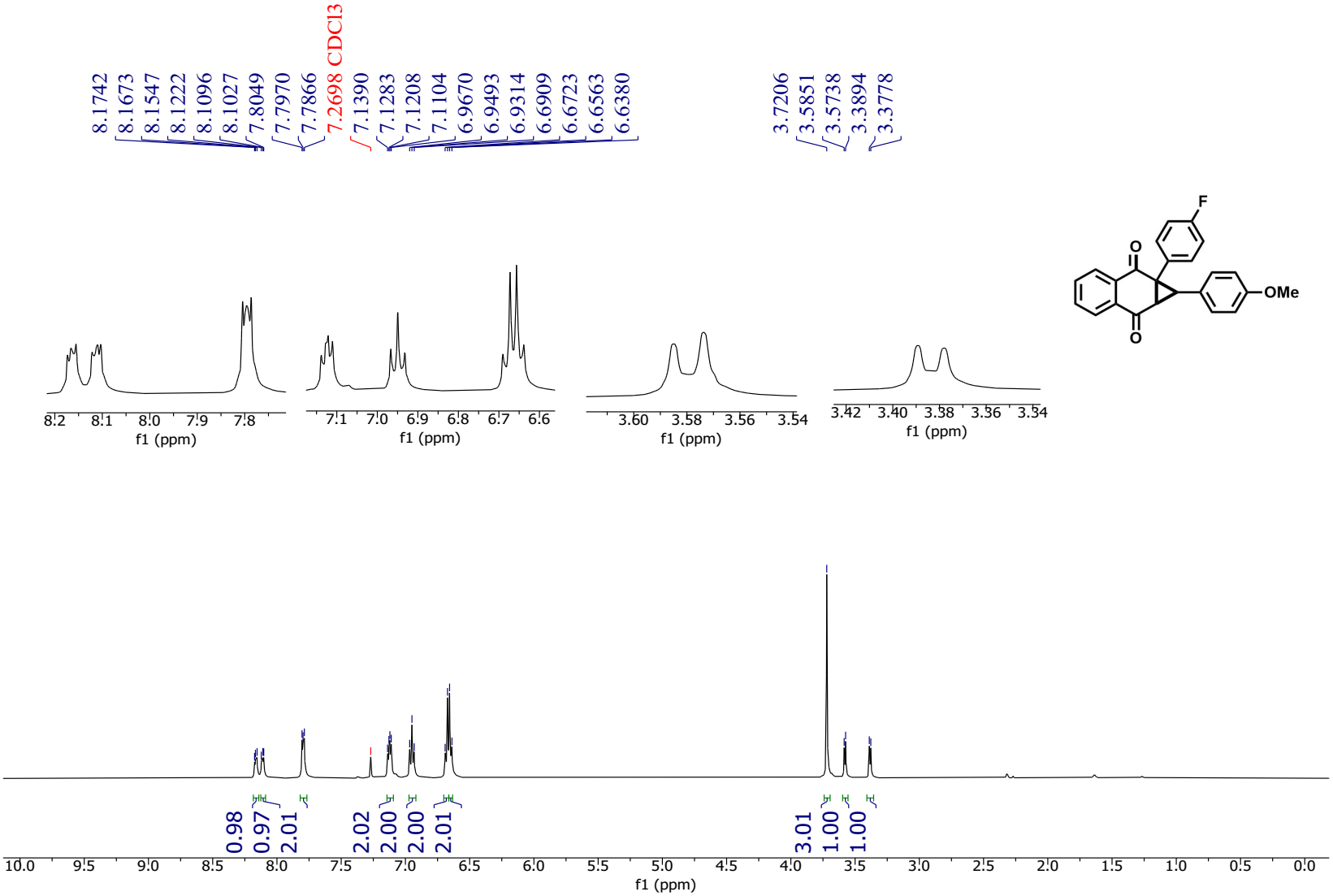
^{19}F NMR (282 MHz, $CDCl_3$) spectrum of **2q**



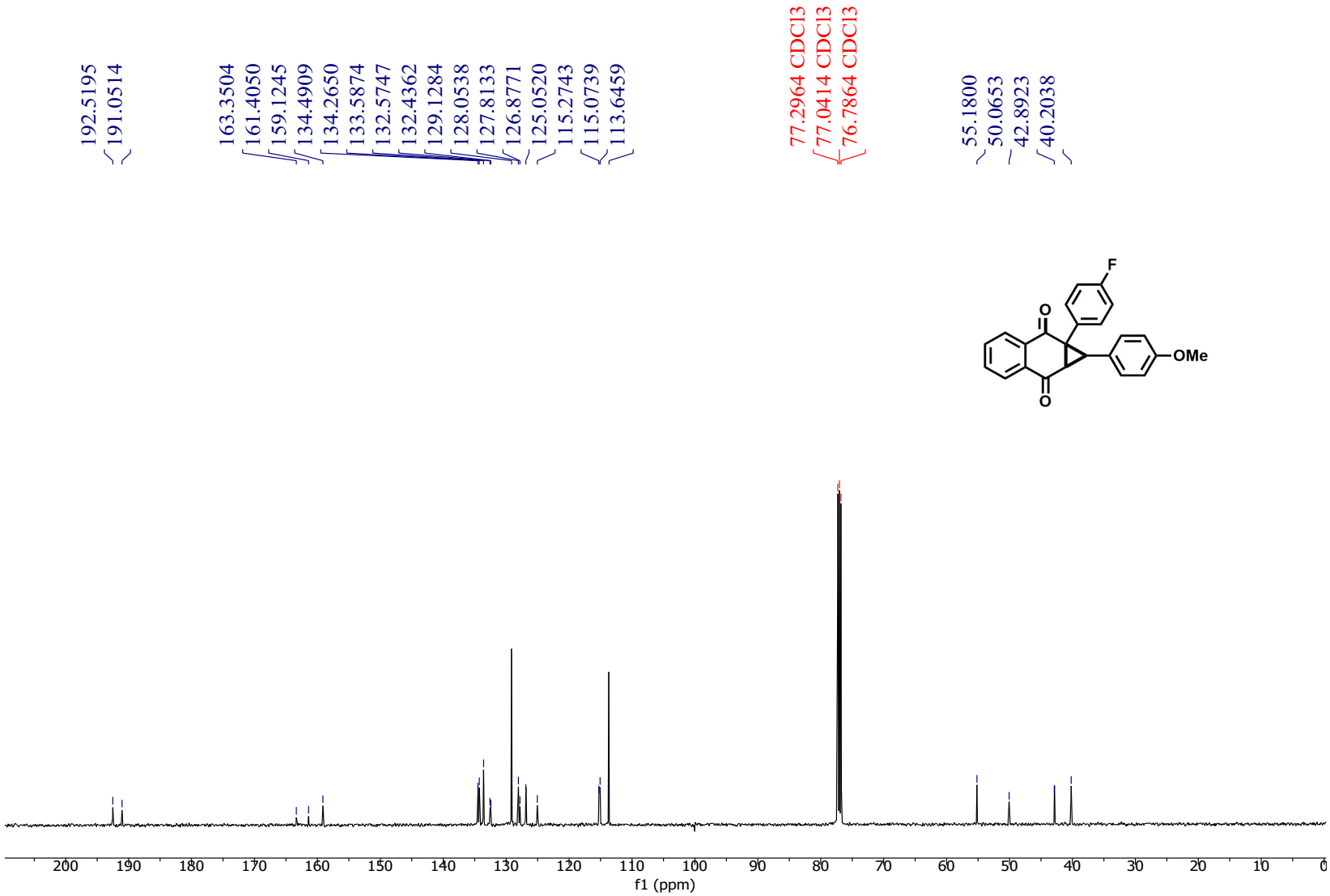
HRMS-ESI Compound **2q**



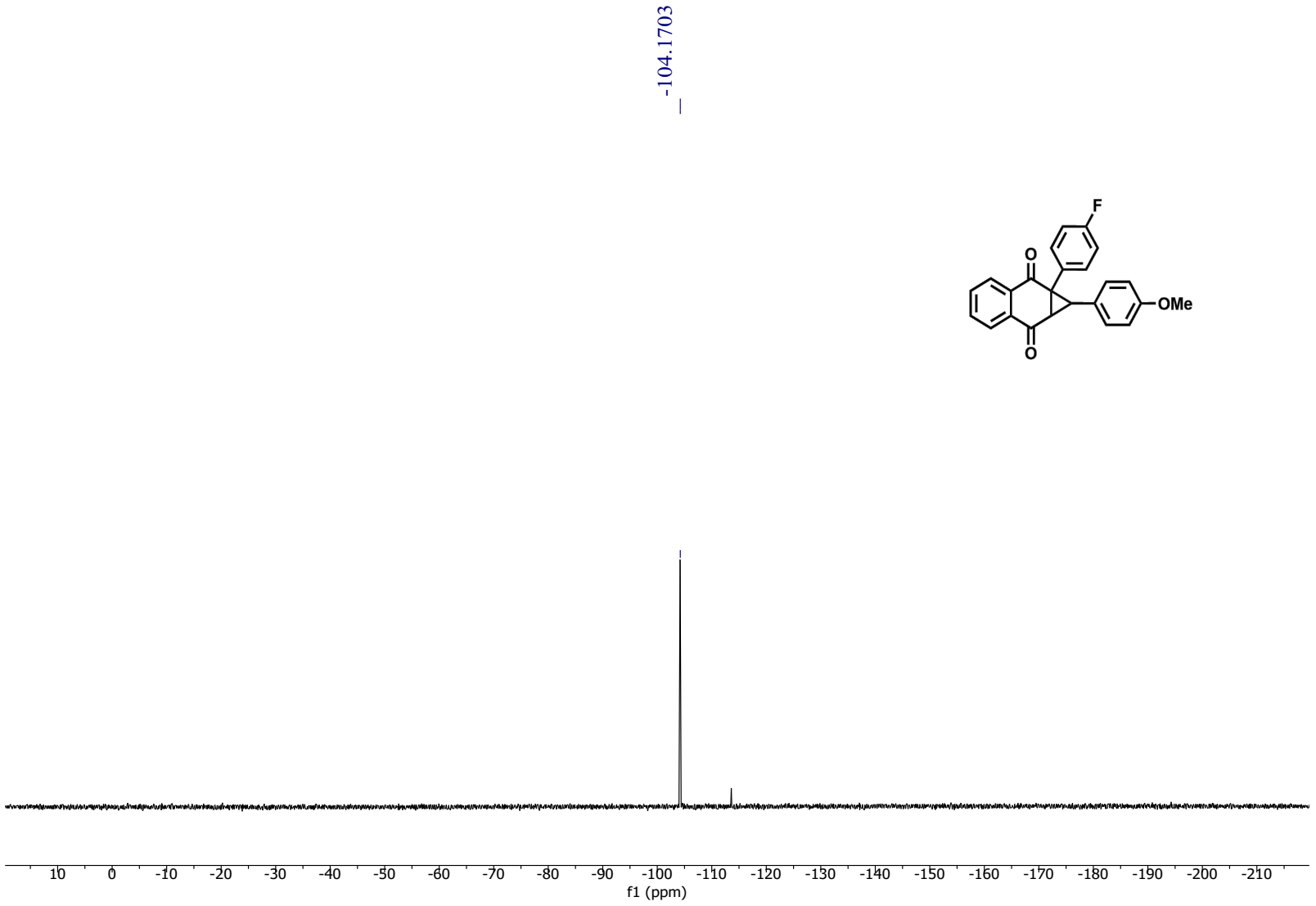
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2r**



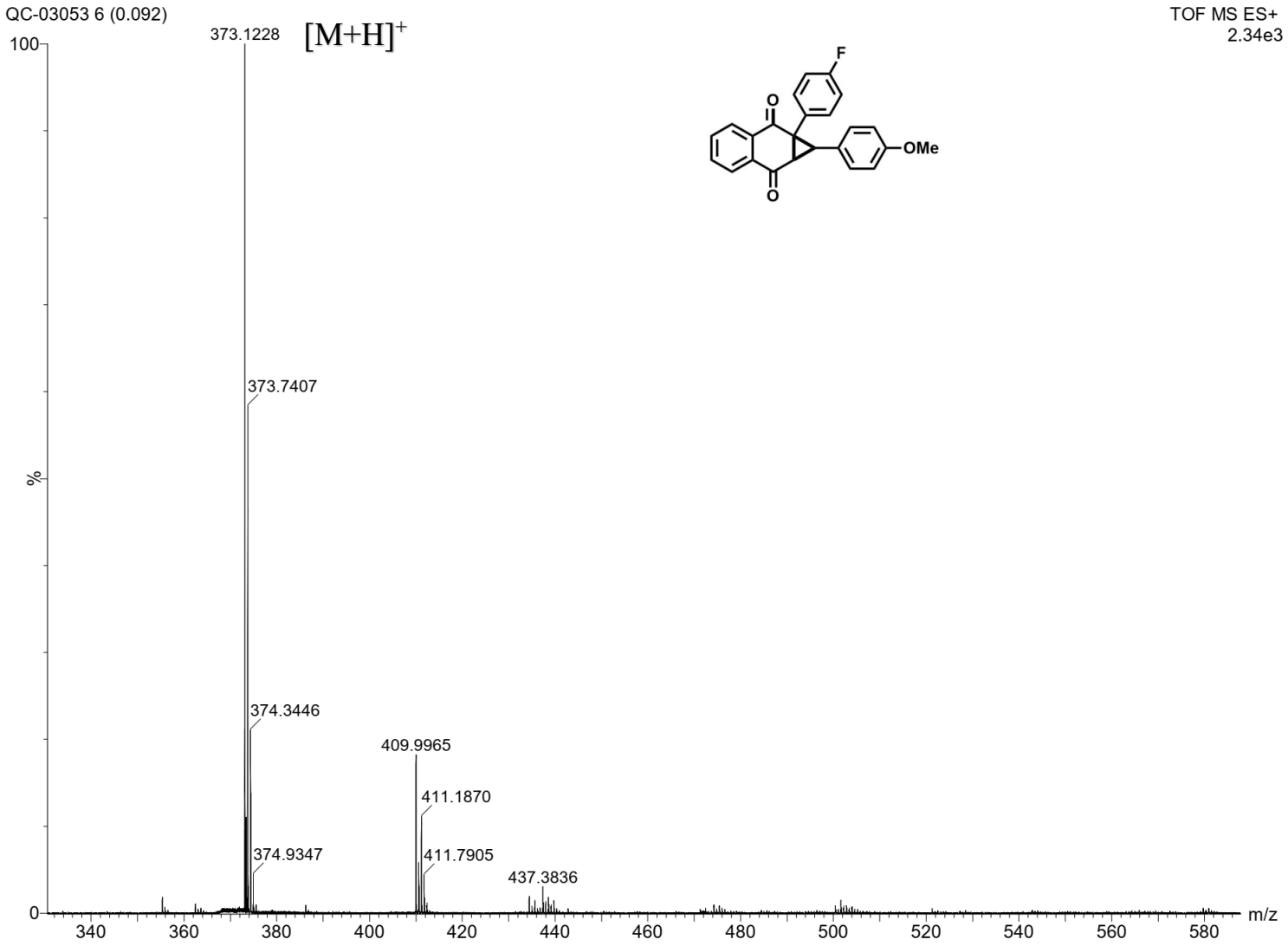
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **2r**



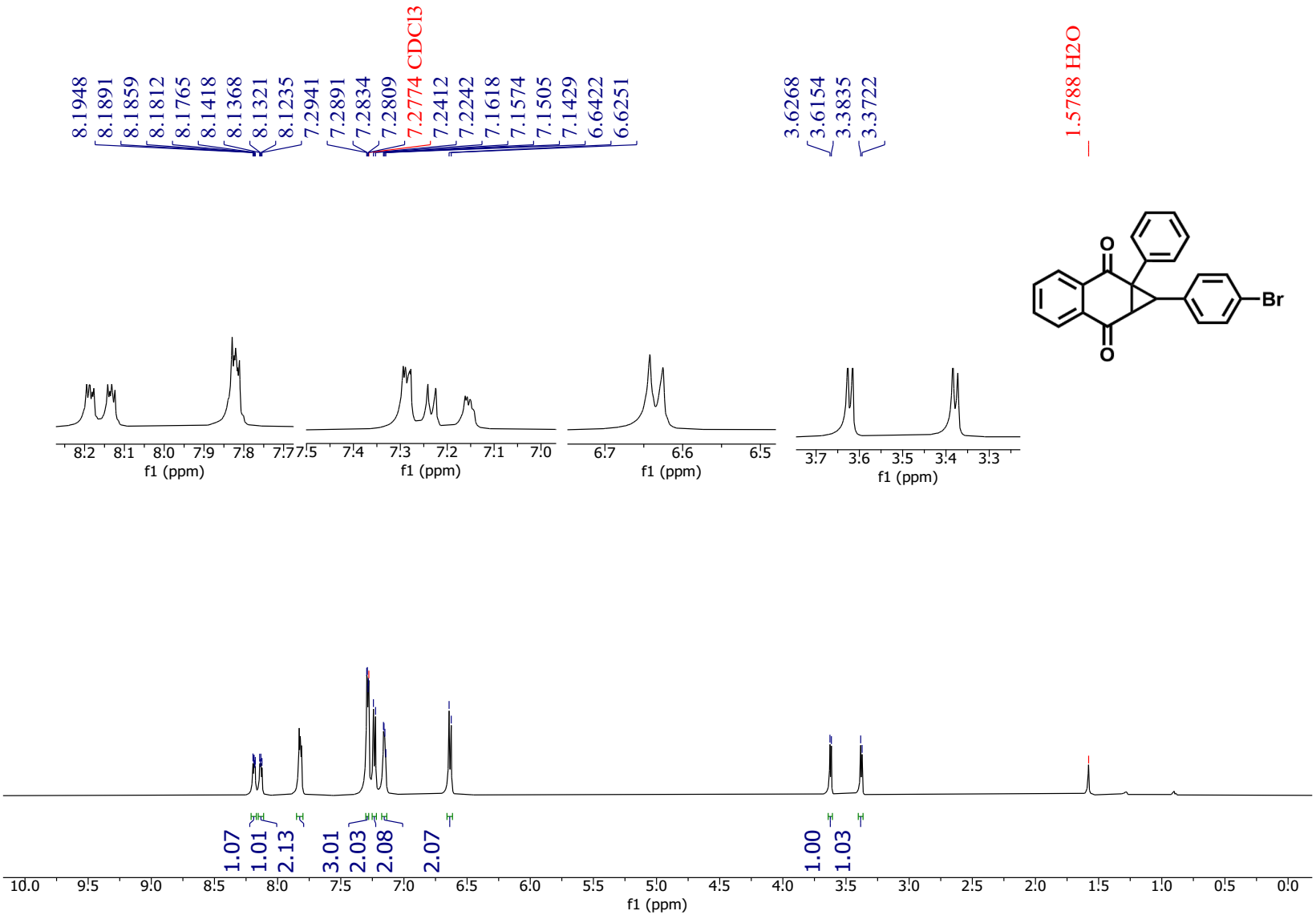
^{19}F NMR (282 MHz, $CDCl_3$) spectrum of **2r**



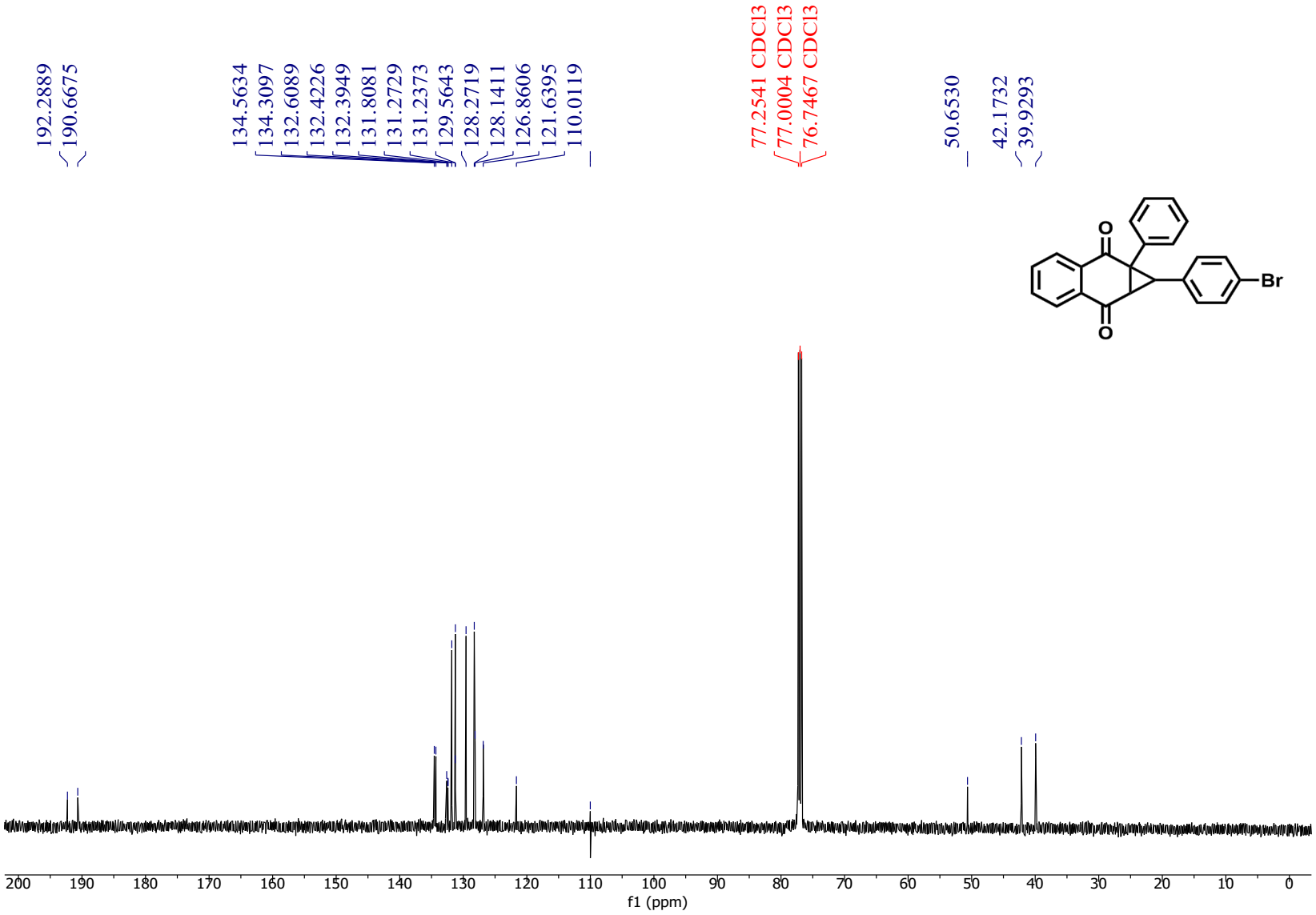
HRMS-ESI Compound **2r**



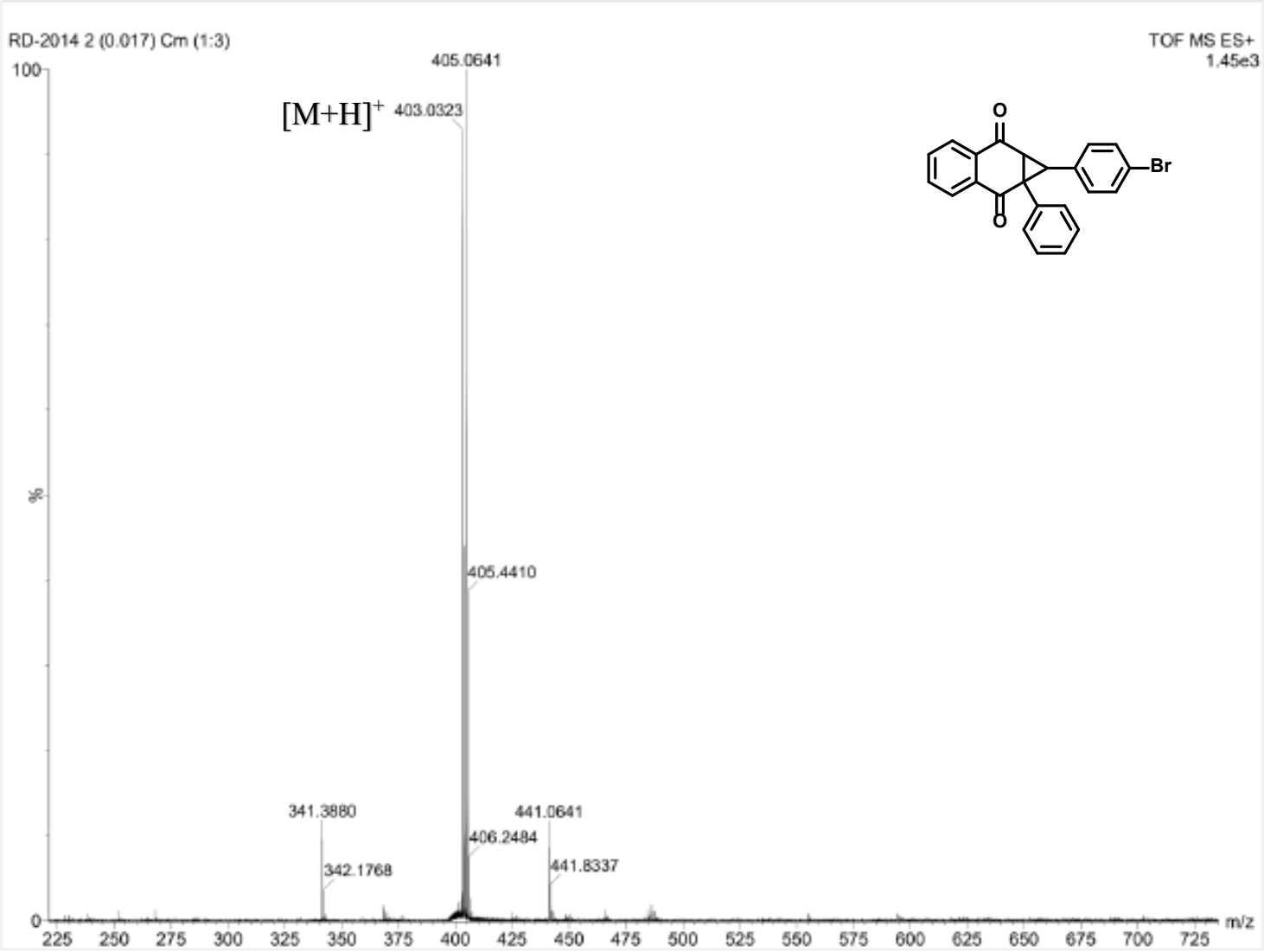
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2s**



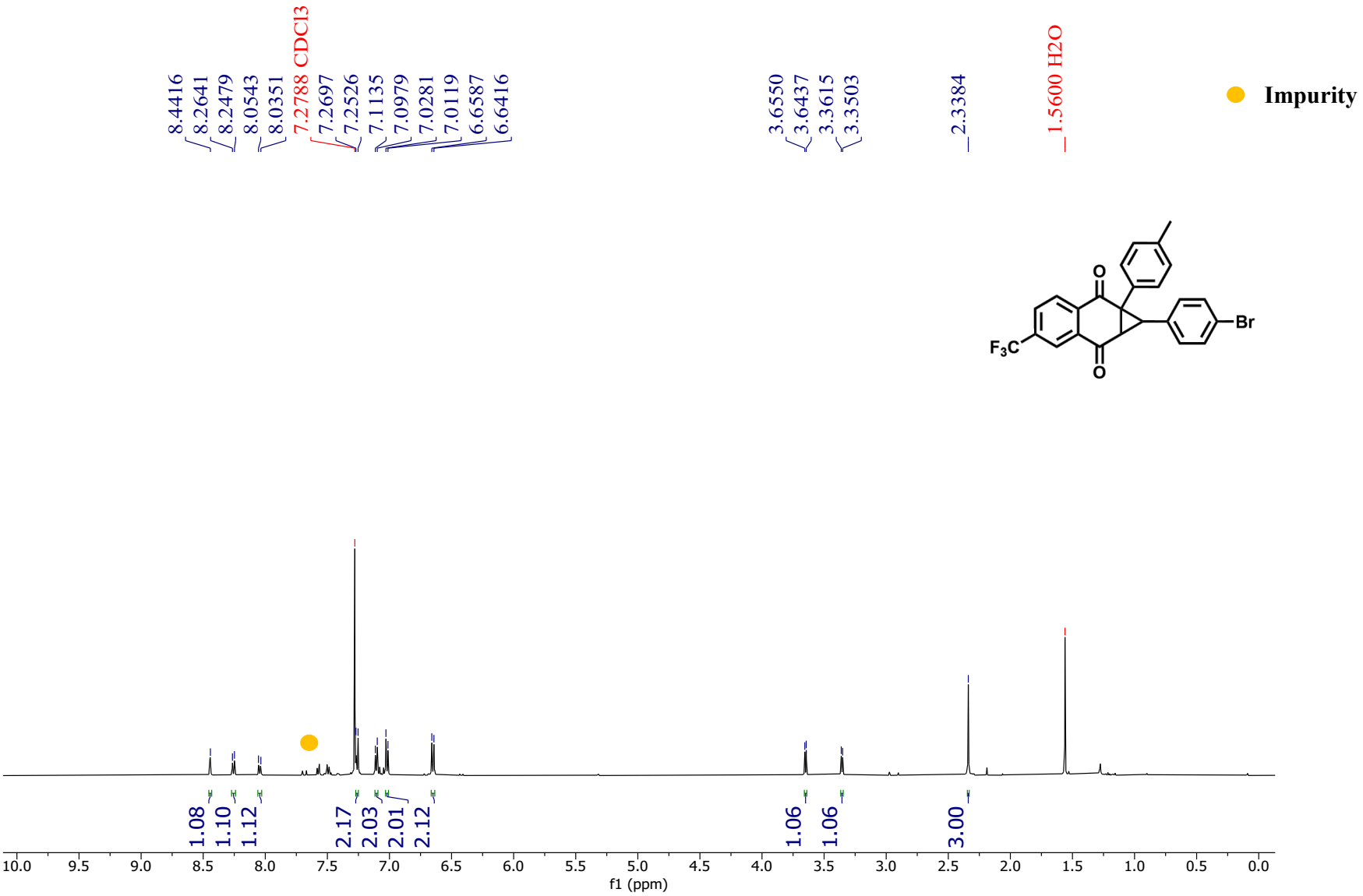
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **2s**



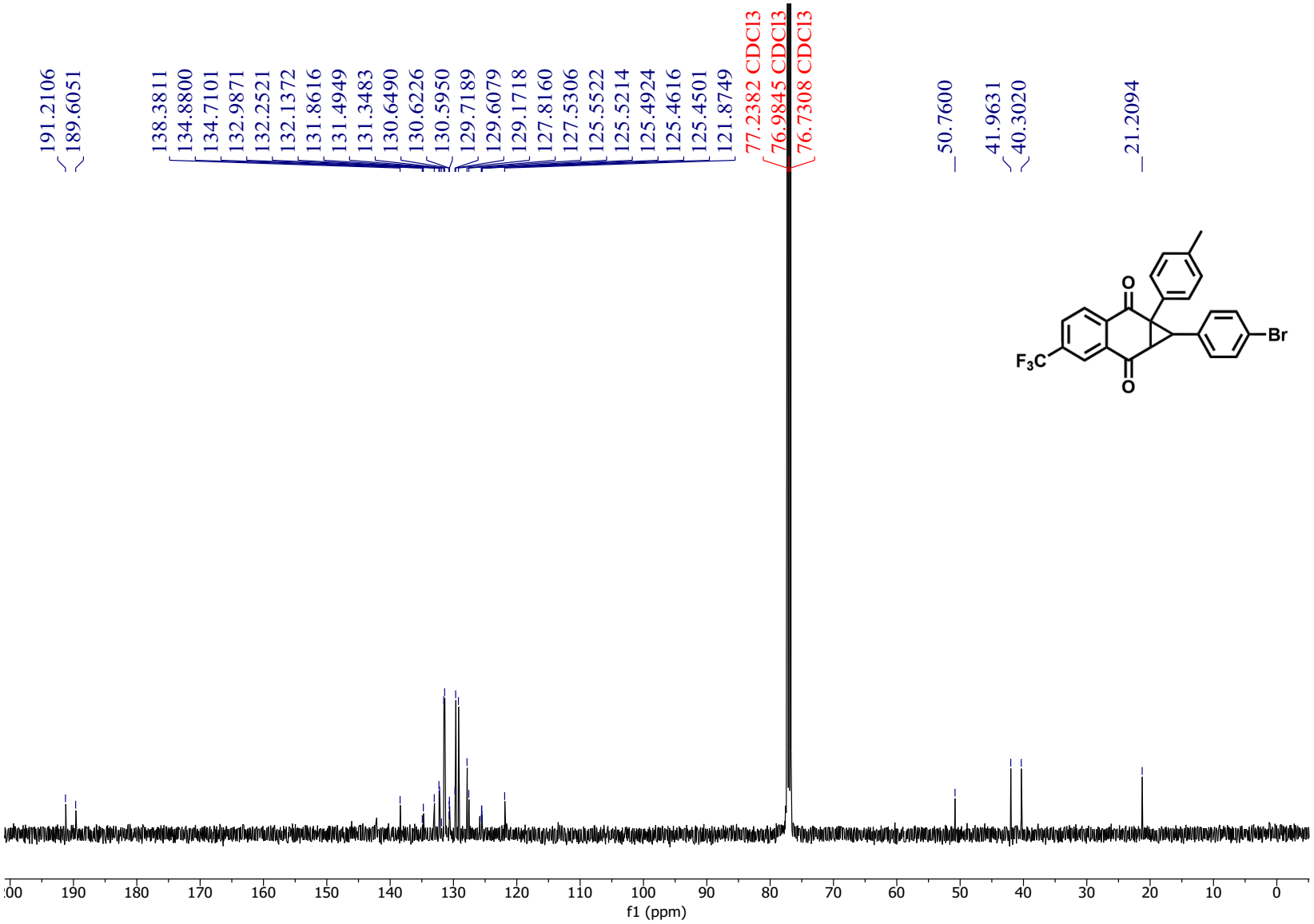
HRMS-ESI Compound **2s**



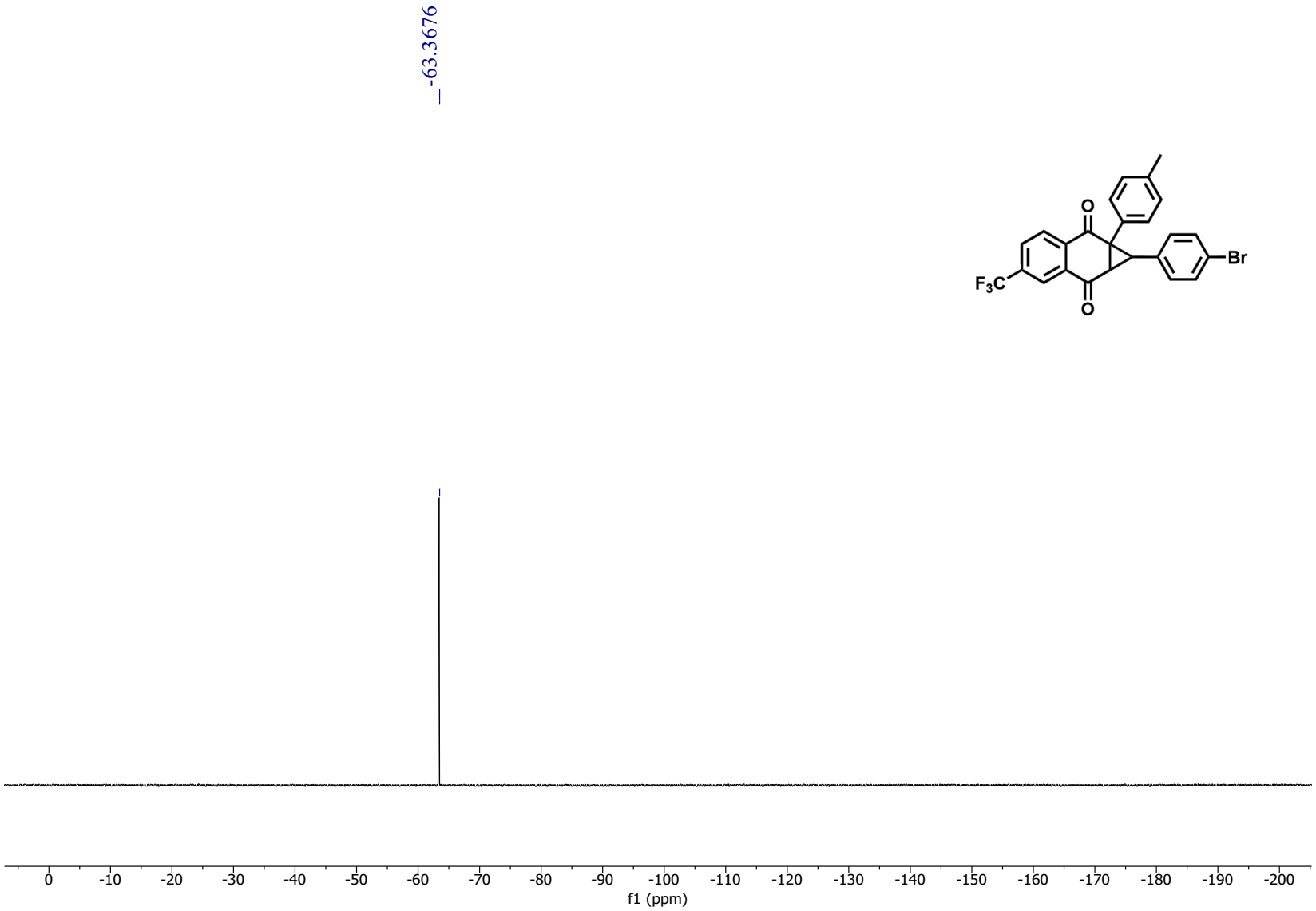
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2t**



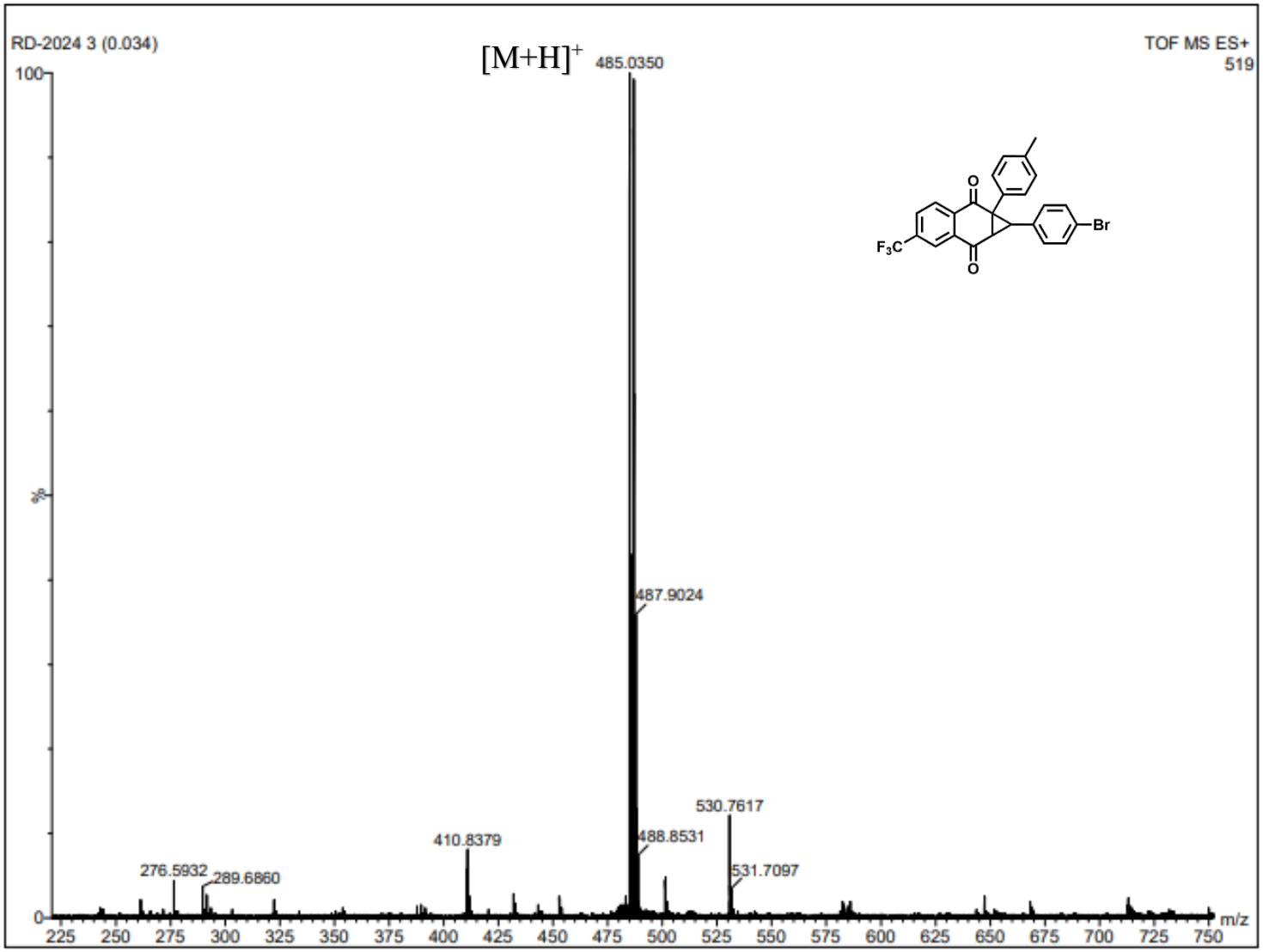
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **2t**



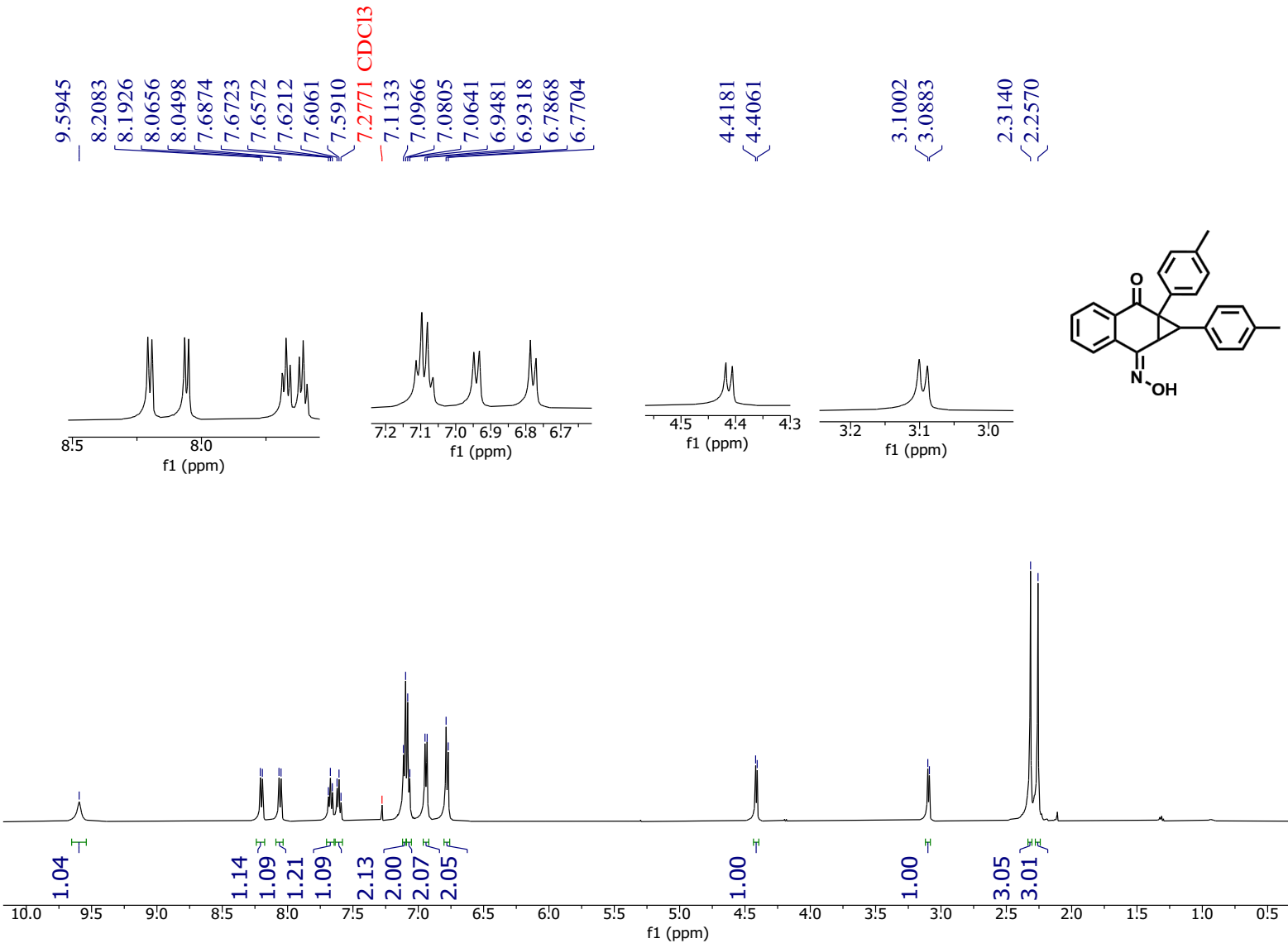
^{19}F NMR (470 MHz, $CDCl_3$) spectrum of **2t**



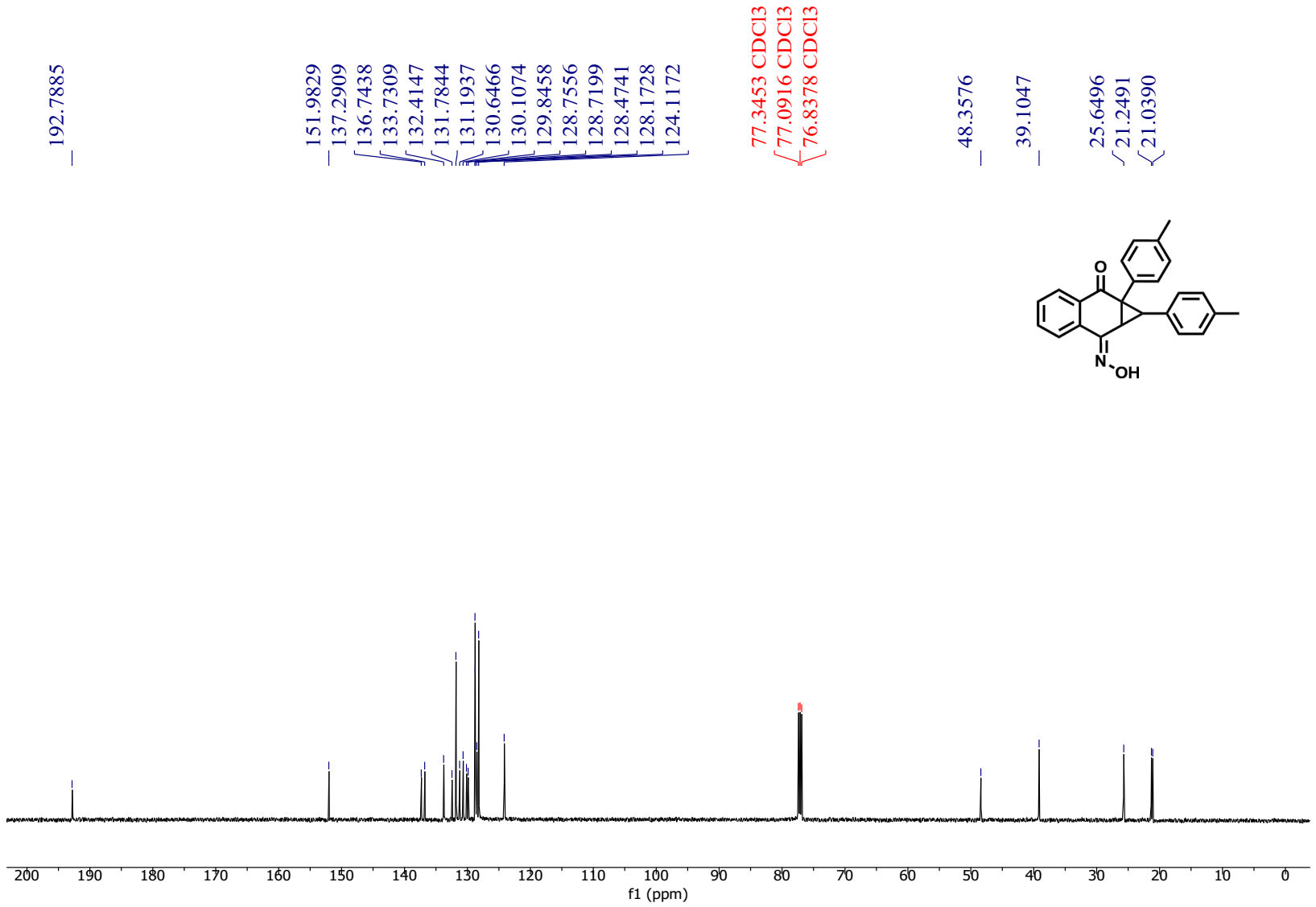
HRMS-ESI Compound **2t**



^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3g**



^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **3g**



HRMS-ESI Compound **3g**