*Cp*Co(III)-Catalyzed C–H Amination/Annulation Cascade of Sulfoxonium Ylides with Anthranils for the Synthesis of Indoloindolones*

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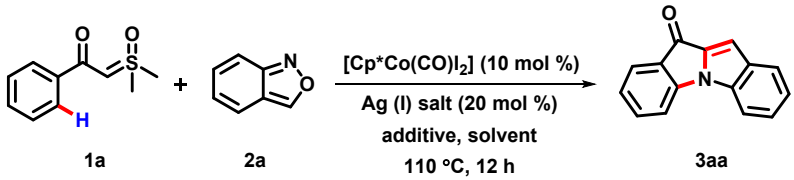
1. General Methods

Unless otherwise stated, all commercial reagents and solvents were used without additional purification. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F254 plates. Visualization via TLC was achieved by the use of UV light (254 nm). Column chromatography was undertaken on silica gel (100−200 mesh) using a proper eluent system. NMR spectra were recorded in chloroform-d at 300, 400 or 500 MHz for ^{1}H NMR spectra and 75, 100 or 125 MHz for ^{13}C NMR spectra. Chemical shifts are quoted in parts per million referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, m = multiplet. Coupling constants, *J*, are reported in hertz. For ^{13}C NMR, chemical shifts are reported in parts per million referenced to the center of a triplet at 77.0 ppm of chloroform-d. HRMS spectra were recorded using ESI-TOF techniques. The sulfoxonium ylides[1] and anthranils[2] were prepared according to the procedure described in the literature.

2. Experimental Procedure of the Optimization Study

To a screw capped vial with a spinvane triangular-shaped Teflon stirbar were added Sulfoxonium ylide **1a** (19.6 mg, 0.10 mmol), Anthranil **2a** (17.9 mg, 0.15 mmol), [Cp*Co(CO)I_2] (4.8 mg, 10 mol %), additive, and solvent (0.6 mL) under N_2 atmosphere. The reaction mixture was stirred at 110 °C for 12 h. After indicated time, cooled to room temperature and the reaction mixture was filtered through a pad of celite and the celite pad was washed with CH_2Cl_2 (10 mL × 2). Solvents were removed under reduced pressure and crude yield was measured by ^{1}H NMR using an internal standard (1,1,2,2-tetrachloroethane).

Table S1. *Optimization of the Co-Catalyzed C−H Functionalization of Sulfoxonium Ylides*[a]



1a 2a 3aa

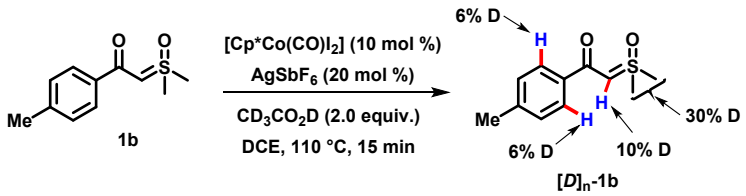
Entry	Ag(I) salt (20 mol %)	Additive (equiv.)	Solvent	Yield (%)[b]
1	$AgSbF_6$	-	DCE	n.d.
2	$AgSbF_6$	NaOAc (2.0)	DCE	n.d.
3	$AgSbF_6$	KOAc (2.0)	DCE	n.d.
4	$AgSbF_6$	AcOH (2.0)	DCE	58
5	$AgSbF_6$	$PhCO_2H$ (2.0)	DCE	48
6	$AgSbF_6$	PivOH (2.0)	DCE	65
7	$AgSbF_6$	$AdCO_2H$ (2.0)	DCE	70
8	$AgNTf_2$	$AdCO_2H$ (2.0)	DCE	62
9	AgOTf	$AdCO_2H$ (2.0)	DCE	54
10[c]	$AgSbF_6$	$AdCO_2H$ (2.0)	DCE	91
11[c]	$AgSbF_6$	$AdCO_2H$ (1.0)	DCE	89
12[c]	$AgSbF_6$	$AdCO_2H$ (1.0)	MeOH	n.d.
13[c]	$AgSbF_6$	$AdCO_2H$ (1.0)	Toluene	43
14[c]	$AgSbF_6$	$AdCO_2H$ (1.0)	1,4-Dioxane	trace
15[c,d]	-	$AdCO_2H$ (1.0)	DCE	65
16[c,e]	$AgSbF_6$	$AdCO_2H$ (1.0)	DCE	n.d.
17[c]	-	$AdCO_2H$ (1.0)	DCE	n.d.

[a]Reaction conditions: **1a** (0.10 mmol), **2a** (0.15 mmol), [Cp*Co(CO)I_2] (10 mol %), Ag (I) Salt (20 mol %) and additive in solvent (0.6 mL) at 100 °C for 12 h. [b]Yields are based on crude ^{1}H NMR (internal standard: 1,1,2,2 tetrachloroethane). [c]Reaction run at 110 °C. [d]Using [Cp*Co(MeCN)$_3$]$(SbF_6)_2$ (10 mol %). [e]Without [Cp*Co(CO)I_2]. n.d. = not detected. $AdCO_2H$ = 1-Admantanecarboxylic acid

3. H/D Exchange Experiment

Cobalt-Catalyzed H/D Exchange in Sulfoxonium ylide 1b with CD_3COOD as an additive in the absence of 2a.

To a dried screw capped vial with a spinvane triangular-shaped Teflon stirbar were added **1b** (21.0 mg, 0.10 mmol), [Cp*Co(CO)I_2] (4.8 mg, 10 mol %), $AgSbF_6$ (6.8 mg, 20 mol %), CD_3COOD (2.0 equiv) and 1,2-DCE (0.6 mL) under N_2 atmosphere. The reaction mixture was stirred at 110 °C for 15 min, cooled to room temperature, filtered through a pad of celite and the celite pad was washed with CH_2Cl_2 (10 mL × 2). The solvent was removed under reduced pressure and the crude residue was purified by column chromatography on silica gel to furnish the product **$[D]_n$-1b** (16 mg, 81%) and the extents of deuterium incorporation was measured by ^1H NMR analysis.



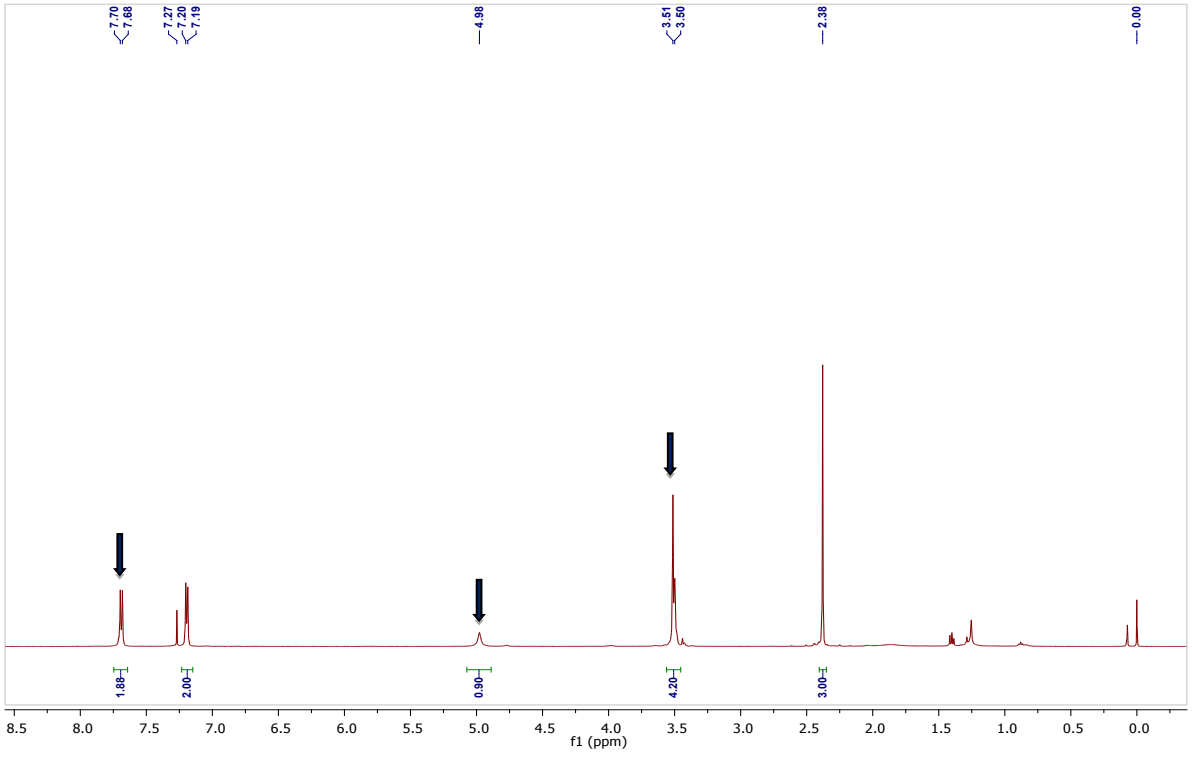
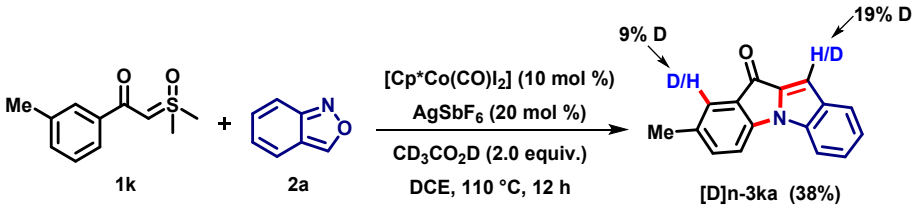


Figure S1. Crude ^1H NMR for H/D exchange experiment of **1b** with CD_3COOD in absence of **2a**

3. H/D Exchange Experiment

Cobalt-Catalyzed H/D Exchange in Sulfoxonium ylide 1k with CD_3COOD as an additive in the presence of 2a.

To a dried screw capped vial with a spinvane triangular-shaped Teflon stirbar were added **1k** (63.0 mg, 0.30 mmol), anthranil **2a** (53.6 mg, 0.45 mmol), [Cp*Co(CO)I_2] (14.4 mg, 10 mol %), $AgSbF_6$ (20.4 mg, 20 mol %), $AdCO_2H$ (54.0 mg, 1.0 equiv), CD_3CO_2D (38.4 mg, 2 equiv) and 1,2-DCE (2.0 mL) under N_2 atmosphere. The reaction mixture was stirred at 110 °C for 12 h, cooled to room temerature, filtered through a pad of celite and then washed with EtOAc (10 mL × 3). The solvent was removed under reduced pressure and the crude residue was purified by column chromatography on silica gel to furnish the product **$[D]_n$-3ka** (27 mg, 38 %) and the extents of deuterium incorporation was measured by ^{1}H NMR analysis.



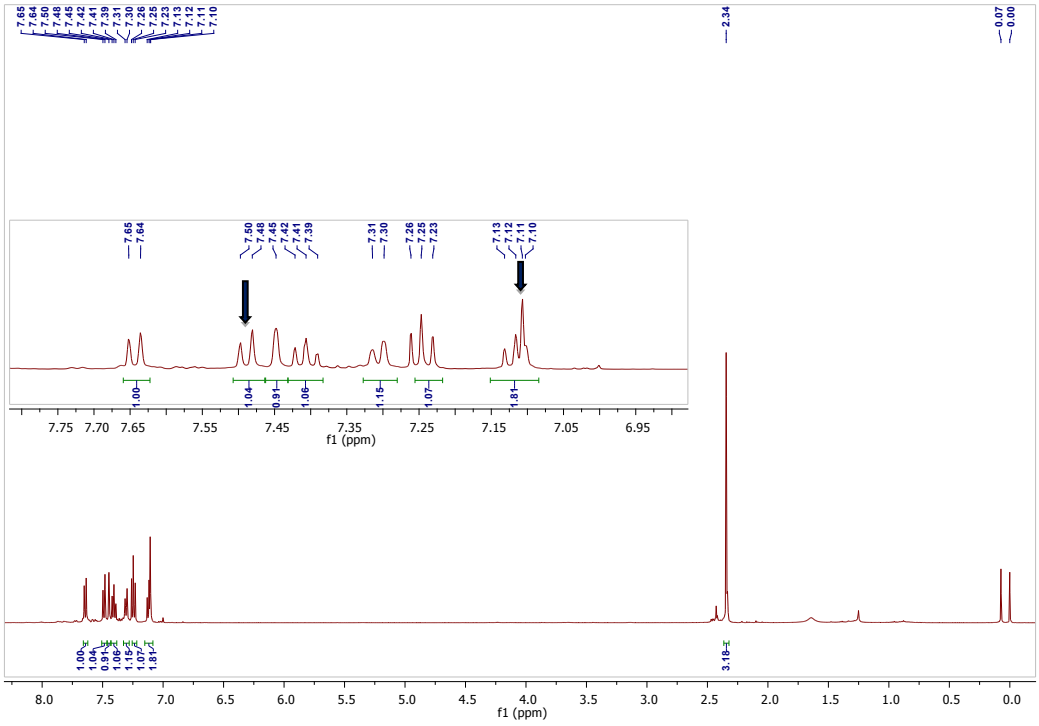
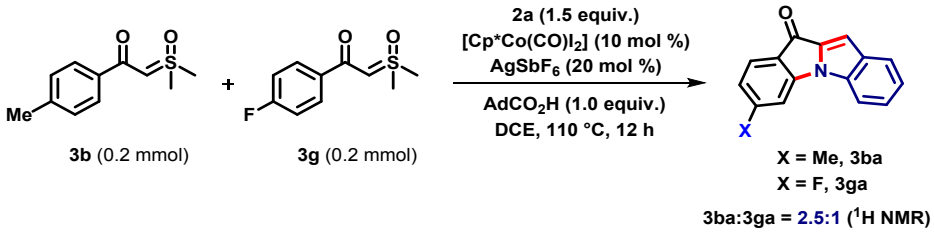


Figure S2. ^{1}H NMR for H/D exchange experiment of **1k** with CD_3COOD in presence of **2a**

4. Intermolecular Competitive Experiment



To a dried screw capped vial with a spinvane triangular-shaped Teflon stirbar were added **3b** (42.0 mg, 0.20 mmol), **3g** (42.9 mg, 0.20 mmol), anthranil **2a** (35.7 mg, 0.30 mmol), [Cp*Co(CO)I_2] (9.6 mg, 10 mol %), $AgSbF_6$ (13.6 mg, 20 mol %), $AdCO_2H$ (36.0 mg, 1.0 equiv) and 1,2-DCE (1.2 mL) under N_2 atmosphere. The reaction mixture was stirred in a pre-heated oil bath at 110 °C for 12 h. The reaction mixture was cooled to room temperature, filtered through a pad of celite and then the celite pad was washed with CH_2Cl_2 (15 mL × 2). The combined organic layers were removed under reduced pressure. The crude residue was purified by column chromatography on silica gel and ratio of the products **3ba** and **3ga** was measured by ^{1}H NMR analysis which was found to be 2.5:1.

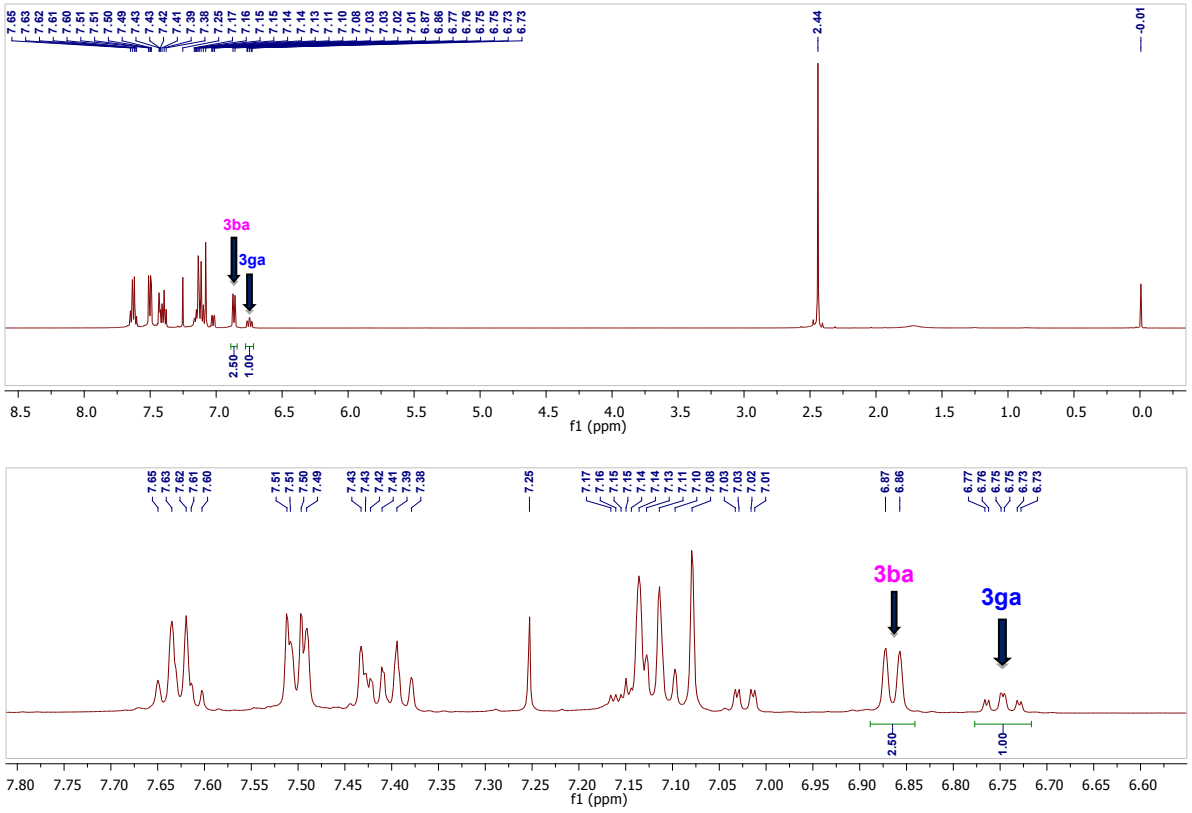
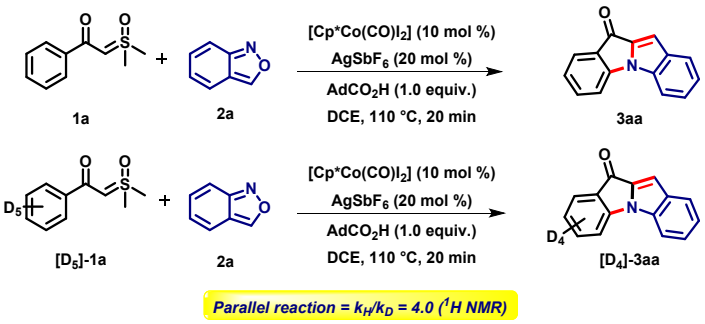


Figure S3. ^{1}H NMR for intermolecular competitive experiment between **3b** and **3g**

5. Intermolecular Kinetic Isotope Effect Experiments (Scheme 5c)

a) The Parallel Reaction.



Sulfoxonium ylide **1a** (19.6 mg, 0.10 mmol) or Sulfoxonium ylide-d_5 **[D5]-1a** (20.1 mg, 0.10 mmol) were added to two separate screw capped vials with spinvane triangular-shaped Teflon stirbar followed by anthranil **2a** (17.9 mg, 0.15 mmol), [Cp*Co(CO)I_2] (4.8 mg, 10 mol %), $AgSbF_6$ (6.8 mg, 20 mol %), $AdCO_2H$ (18.0 mg, 1.0 equiv) and 1,2-DCE (0.6 mL) under N_2 atmosphere. These two reaction mixtures were stirred side-by-side at 110 °C for 20 min. Then, these two mixtures were rapidly combined and and the combined mixture was poured into water (20 mL) and extracted with EtOAc (2 × 15 mL). The combined organics were dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography to afford the desired **3aa** and **[D4]-3aa**. **KIE = 4.0.**

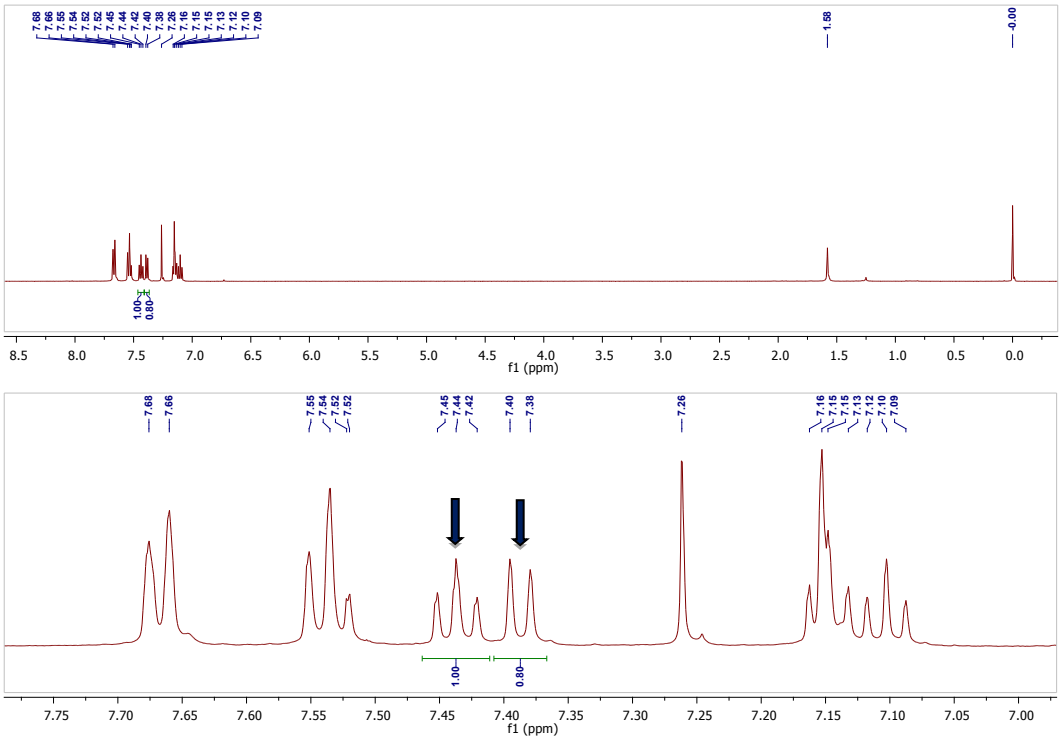
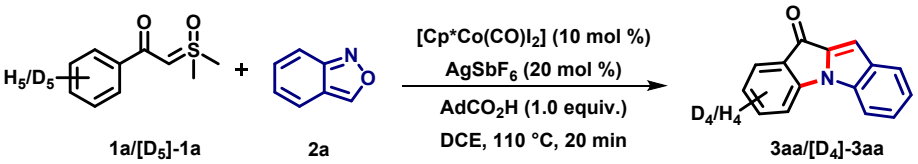


Figure S4. ^{1}H NMR for KIE Study **(Parallel Reactions)**

5. Kinetic Isotope Effect Experiments (Scheme 5c)

a) The Competitive Reaction



***Competitive reaction* = k_H/k_D = 4.3 (^{1}H NMR)**

To a dried screw capped vial with a spinvane triangular-shaped Teflon stirbar were added **1a** (19.6 mg, 0.10 mmol), **[D_5]-1a** (20.1 mg, 0.10 mmol), anthranil **2a** (17.9 mg, 0.15 mmol), [Cp*Co(CO)I_2] (4.8 mg, 10 mol %) , $AgSbF_6$ (6.8 mg, 20 mol %), $AdCO_2H$ (18.0 mg, 1.0 equiv) and 1,2-DCE (0.6 mL) under N_2 atmosphere. The reaction mixture was heated at 110 °C for 20 min. The reaction mixture was cooled to room temperature and diluted with water (20 mL) and extracted with EtOAc (2 × 15 mL). The combined organics were dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography to afford the desired **3aa** and **[D4]-3aa**. **KIE = 4.3**.

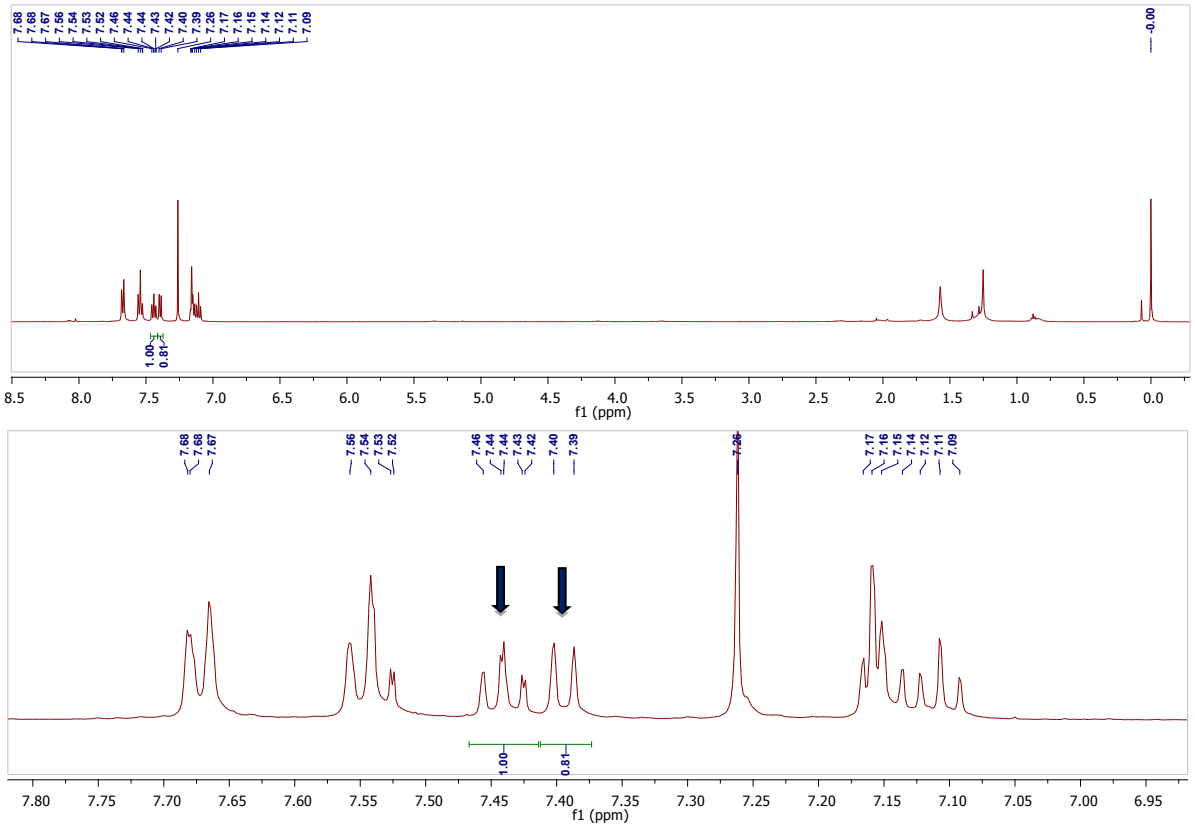


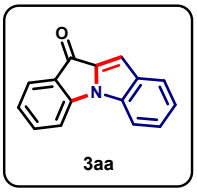
Figure S5. ^{1}H NMR for KIE Study **(Competitive Reaction)**

6. General Procedure for the Co-Catalyzed C–H Amination/Annulation Cascade for the Synthesis of Indoloindolones.

To a screw capped seal tube vial with a Teflon stirbar were added sulfoxonium ylide **1** (0.30 mmol), anthranil **2** (0.45 mmol, 1.5 equiv), [Cp*Co(CO)I_2] (14.4 mg, 10 mol %), $AdCO_2H$ (54.0 mg, 1.0 equiv.), and 1,2-DCE (2.0 mL) under N_2 atmosphere. The reaction mixture was stirred at 110 °C for 12 h, filtered through a pad of celite and then the celite pad was washed with CH_2Cl_2 (20 mL × 2). The solvents were removed under reduced pressure and the residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc) to give the desired Indoloindolones derivatives.

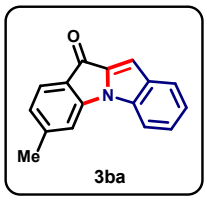
7. Spectroscopic Data of Indoloindolones Obtained in this Study

10*H*-Indolo[1,2-*a*]indol-10-one (3aa).[3]



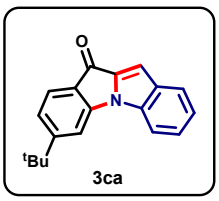
Yellow solid (55.0 mg, 84%); m.p. 160 – 162 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.63 (d, *J* = 7.9 Hz, 2H), 7.54 – 7.45 (m, *J* = 7.8 Hz, 2H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.16 – 7.01 (m, 2H), 7.07 (t, *J* = 7.5 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 181.6, 145.5, 135.8, 135.5, 134.3, 132.6, 129.4, 128.1, 125.1, 125.0, 123.8, 121.9, 111.3, 108.0.

7-Methyl-10*H*-indolo[1,2-*a*]indol-10-one (3ba).[3]



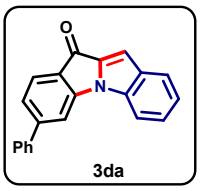
Yellow solid (60.0 mg, 85%); m.p. 175 – 177 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.63 (d, *J* = 8.0 Hz, 1H), 7.57 – 7.47 (m, 2H), 7.41 (d, *J* = 7.4 Hz, 1H), 7.20 – 7.01 (m, 3H), 6.86 (d, *J* = 7.6 Hz, 1H), 2.44 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 181.5, 147.2, 145.9, 136.3, 134.1, 132.6, 127.9, 127.0, 125.0, 124.9, 124.8, 121.8, 112.1, 111.3, 107.6, 22.5.

7-(*tert*-Butyl)-10*H*-Indolo[1,2-*a*]indol-10-one (3ca).



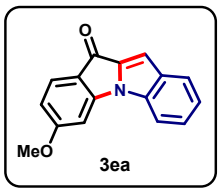
Yellow solid (69.0 mg, 84%); m.p. 147 – 149 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.62 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 8.2 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.36 (s, 1H), 7.20 – 7.01 (m, 3H), 1.40 (s, 9H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 181.5, 160.4, 146.0, 136.3, 134.2, 132.5, 127.8, 126.9, 124.9, 124.8 121.8, 121.0, 111.3, 108.6, 107.5, 35.8, 31.0; **HRMS (ESI)** m/z calcd. for $C_{19}H_{17}NONa$ $[M+Na]^+$: 298.1208, found: 298.1203.

7-Phenyl-10*H*-indolo[1,2-*a*]indol-10-one (3da).



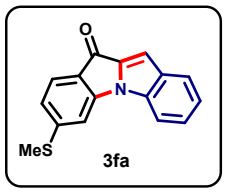
Yellow solid (54.0 mg, 61%); m.p. 149 – 151 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.72 (d, *J* = 7.9 Hz, 1H), 7.70 – 7.65 (m, 3H), 7.61 (d, *J* = 8.3 Hz, 1H), 7.56 (s, 1H), 7.52 (t, *J* = 7.4 Hz, 2H), 7.49 – 7.41 (m, 2H), 7.31 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.19 – 7.12 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 181.3, 149.1, 146.2, 140.0, 136.4, 134.3, 132.7, 129.1, 128.8, 128.2, 128.1, 127.3, 125.5, 125.1, 122.9, 122.0, 111.4, 110.2, 108.0; **HRMS (ESI)** m/z calcd. for $C_{21}H_{13}NONa$ $[M+Na]^+$: 318.0895, found: 318.0889.

7-Methoxy-10*H*-indolo[1,2-*a*]indol-10-one (3ea).[3]



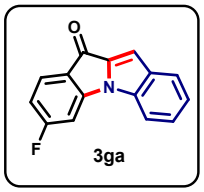
Yellow solid (72.0 mg, 72%); m.p. 186 – 188 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.62 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.43 (dd, *J* = 8.3, 0.8 Hz, 1H), 7.38 (ddd, *J* = 8.2, 7.1, 1.1 Hz, 1H), 7.11 (ddd, *J* = 8.0, 7.2, 0.9 Hz, 1H), 7.05 (d, *J* = 0.6 Hz, 1H), 6.81 (d, *J* = 2.1 Hz, 1H), 6.52 (dd, *J* = 8.4, 2.1 Hz, 1H), 3.91 (s, 3H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ 180.5, 166.1, 147.4, 136.9, 134.0, 132.6, 127.7, 126.8, 124.8, 122.5, 121.9, 111.1, 107.9, 107.2, 98.6, 55.9.

7-(methylthio)-10*H*-Indolo[1,2-*a*]indol-10-one (3fa).



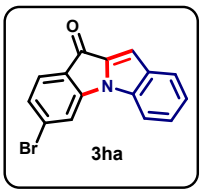
Yellow solid (59.0 mg, 74%); m.p. 187 – 189 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** 7.66 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 8.2 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.18 (s, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.12 (s, 1H), 6.87 (d, *J* = 7.9 Hz, 1H), 2.60 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 180.6, 149.5, 145.7, 136.4, 134.0, 132.6, 127.9, 125.9, 125.1, 124.9, 122.0, 119.4, 111.2, 107.8, 107.7, 15.0; **HRMS (ESI)** m/z calcd. for $C_{16}H_{11}NOSNa$ $[M+Na]^+$: 288.0459, found: 288.0453.

7-Fluoro-10*H*-indolo[1,2-*a*]indol-10-one (3ga).[3]



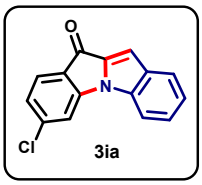
Yellow solid (41.0 mg, 58%); m.p. 203 – 205 °C; **H NMR (500 MHz, $CDCl_3$)** δ 7.69 – 7.59 (m, 2H), 7.51 – 7.39 (m, 2H), 7.19 – 7.13 (m, 1H), 7.13 (s, 1H), 7.04 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.81 – 6.70 (m, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 180.0, 167.6 (d, $J_{C\text{-}F}$ = 255.6 Hz), 147.0 (d, $J_{C\text{-}F}$ = 13.1 Hz), 136.3, 134.1, 132.6, 128.3, 127.1 (d, $J_{C\text{-}F}$ = 11.2 Hz), 125.6, 125.1, 122.4, 111.1, 110.6 (d, $J_{C\text{-}F}$ = 23.3 Hz), 108.5, 100.0 (d, $J_{C\text{-}F}$ = 28.0 Hz).

7-Bromo-10*H*-indolo[1,2-*a*]indol-10-one (3ha).



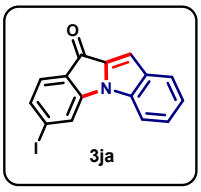
Yellow solid (58.0 mg, 65%); m.p. 204 – 206 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.66 (d, *J* = 8.0 Hz, 1H), 7.52 – 7.46 (m, 3H), 7.47 – 7.41 (m, 1H), 7.23 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.19 – 7.13 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 180.3, 146.0, 135.8, 134.1, 132.7, 130.1, 128.5, 128.2, 126.9, 126.1, 125.2, 122.5, 114.8, 111.3, 108.9; **HRMS (ESI)** m/z calcd. for $C_{15}H_8BrNONa$ $[M+Na]^+$: 319.9687, found: 319.9681.

7-Chloro-10*H*-indolo[1,2-*a*]indol-10-one (3ia).[3]



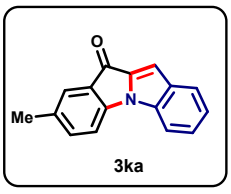
Yellow solid (48.0 mg, 63%); m.p. 217 – 219 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.68 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 8.2 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.37 (s, 1H), 7.23 – 7.14 (m, 2H), 7.08 (d, *J* = 7.7 Hz, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 180.2, 146.1, 141.7, 135.9, 134.1, 132.7, 128.5, 127.8, 126.0, 125.2, 124.0, 122.5, 112.0, 111.3, 108.8.

7-Iodo-10*H*-indolo[1,2-*a*]indol-10-one (3ja).



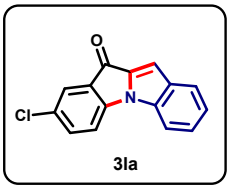
Yellow solid (65.0 mg, 63%); m.p. 199 – 201 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.62 (s, 1H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.46 – 7.31 (m, 3H), 7.26 (d, *J* = 7.5 Hz, 1H), 7.15 – 6.99 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 180.6, 145.7, 135.5, 134.1, 133.1, 132.7, 128.8, 128.5, 126.0, 125.2, 122.4, 120.5, 111.4, 108.8, 102.6; **HRMS (ESI)** m/z calcd. for $C_{15}H_8INONa$ $[M+Na]^+$: 367.9548, found: 367.9542.

8-Methyl-10*H*-indolo[1,2-*a*]indol-10-one (3ka).[3]



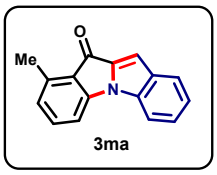
Brick red solid (58.0 mg, 83%); m.p. 129 – 131 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.63 (d, *J* = 8.1 Hz, 1H), 7.48 (d, *J* = 8.3 Hz, 1H), 7.44 (s, 1H), 7.40 (t, *J* = 7.9 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.14 – 7.07 (m, 2H), 2.33 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 181.9, 143.5, 136.0, 135.9, 134.2, 133.7, 132.4, 129.5, 127.9, 125.6, 125.0, 121.7, 111.2, 111.0, 107.6, 20.9.

8-Chloro-10*H*-indolo[1,2-*a*]indol-10-one (3la).[3]



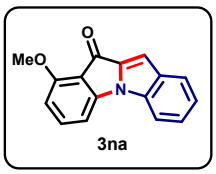
Yellow solid (81.0 mg, 81%); m.p. 203 – 205 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.66 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 1.7 Hz, 1H), 7.55 – 7.40 (m, 3H), 7.29 (d, *J* = 8.3 Hz, 1H), 7.22 – 7.11 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 180.0, 143.7, 135.7, 134.9, 134.2, 132.5, 130.7, 129.5, 128.5, 125.3, 125.2, 122.3, 112.2, 111.2, 108.9.

9-Methyl-10*H*-indolo[1,2-*a*]indol-10-one (3ma).[3]



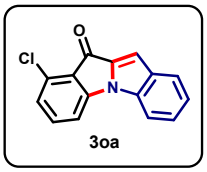
Yellow solid (66.0 mg, 70%); m.p. 158 – 160 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.65 (d, *J* = 8.1 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.44 – 7.39 (m, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.20 (d, *J* = 7.8 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.09 (s, 1H), 6.84 (d, *J* = 7.7 Hz, 1H), 2.63 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 182.9, 145.9, 140.8, 136.0, 134.8, 134.0, 132.6, 127.7, 126.5, 126.4, 124.9, 121.8, 111.4, 108.8, 107.0, 17.7.

9-Methoxy-10*H*-indolo[1,2-*a*]indol-10-one (3na).



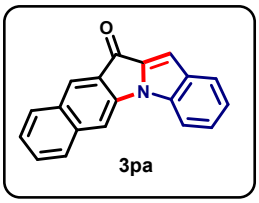
Yellow solid (64.0 mg, 84%); m.p. 163 – 165 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.64 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 8.2 Hz, 1H), 7.46 (t, *J* = 8.1 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.09 (s, 1H), 6.96 (d, *J* = 7.7 Hz, 1H), 6.60 (d, *J* = 8.5 Hz, 1H), 3.98 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 179.9, 158.7, 146.8, 137.5, 135.9, 134.1, 132.6, 127.6, 124.8, 121.8, 116.0, 111.3, 107.3, 107.1, 104.0, 56.0; **HRMS (ESI)** m/z calcd. for $C_{16}H_{11}NO_2Na$ $[M+Na]^+$: 272.0687, found 272.0681.

9-Chloro-10*H*-indolo[1,2-*a*]indol-10-one (3oa).[3]



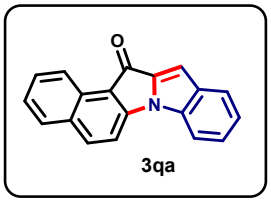
Yellow solid (55.0 mg, 72%); m.p. 208 – 210 °C; **^{1}H NMR 500 MHz, $CDCl_3$)** δ 7.68 (d, *J* = 7.9 Hz, 1H), 7.53 (d, *J* = 8.2 Hz, 1H), 7.49 – 7.40 (m, 2H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.22 – 7.15 (m, 2H), 7.03 (d, *J* = 8.0 Hz, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 178.7, 146.7, 135.9, 135.6, 134.1, 133.2, 132.7, 128.3, 125.6, 125.2, 122.4, 111.4, 109.7, 108.5.

12*H*-Benzo[*f*]indolo[1,2-*a*]indol-12-one (3pa).



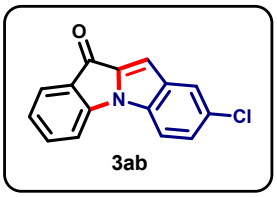
Brick red solid (46.0 mg, 56%); m.p. 218 – 220 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.19 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.79 – 7.69 (m, 2H), 7.63 (s, 1H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.24 – 7.15 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 181.2, 139.7, 137.2, 136.8, 133.9, 132.9, 130.9, 130.3, 129.8, 129.6, 127.9, 126.6, 125.7, 124.9, 122.3, 111.9, 107.4, 106.5; **HRMS (ESI)** m/z calcd. for $C_{19}H_{12}NO$ $[M+H]^+$: 270.0919, found: 270.0912.

13*H*-Benzo[*e*]indolo[1,2-*a*]indol-13-one (3qa).[3]



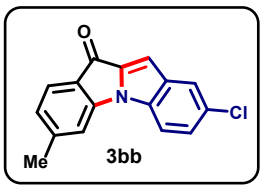
Brick red solid (41.0 mg, 50%); m.p. 197 – 199 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.19 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.63 (s, 1H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.24 – 7.16 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 182.6, 147.1, 137.3, 136.8, 134.8, 132.9, 130.6, 130.0, 128.6, 128.2, 125.3, 125.1, 123.4, 121.9, 120.3, 111.4, 111.1, 108.8.

2-Chloro-10*H*-indolo[1,2-*a*]indol-10-one (3ab).[4]



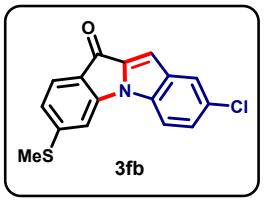
Yellow solid (58.0 mg, 76%); m.p. 199 – 201 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.67 (d, *J* = 7.4 Hz, 1H), 7.64 (s, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 8.7 Hz, 1H), 7.38 (d, *J* = 8.9 Hz, 1H), 7.35 (d, *J* = 7.9 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.07 (s, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 181.3, 145.2, 136.6, 135.7, 133.4, 132.4, 129.1, 128.3, 127.5, 125.3, 124.3, 124.2, 112.1, 111.3, 106.9.

2-Chloro-7-methyl-10*H*-indolo[1,2-*a*]indol-10-one (3bb).



Yellow solid (61.0 mg, 75%); m.p. 188 – 190 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.62 (s, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 8.7 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.14 (s, 1H), 7.03 (s, 1H), 6.92 (d, *J* = 7.5 Hz, 1H), 2.47 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 181.1, 147.4, 145.6, 137.1, 133.4, 132.3, 128.1, 127.3, 126.7, 125.1, 124.9, 124.1, 112.10, 112.05, 106.5, 22.5; **HRMS (ESI)** m/z calcd. for $C_{16}H_{10}ClNONa$ $[M+Na]^+$: 290.0349, found: 290.0343.

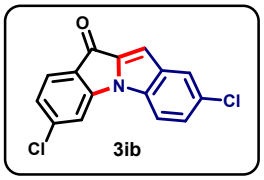
2-Chloro-7-(methylthio)-10*H*-indolo[1,2-*a*]indol-10-one (3fb).



3fb

Yellow solid (64.0 mg, 71%); m.p. 159 – 161 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.65 (s, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.45 (d, *J* = 8.7 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.16 (s, 1H), 7.05 (s, 1H), 6.90 (d, *J* = 7.9 Hz, 1H), 2.61 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 180.4, 149.9, 145.5, 137.4, 133.6, 132.2, 128.2, 127.6, 125.7, 125.3, 124.2, 119.7, 112.1, 107.8, 106.7, 15.1; **HRMS (ESI)** m/z calcd. for $C_{16}H_{11}ClNOS$ $[M+H]^+$: 322.0069, found: 322.0063.

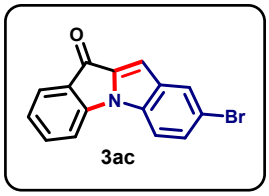
2,7-Dichloro-10*H*-indolo[1,2-*a*]indol-10-one (3ib).



3ib

Yellow solid (61.0 mg, 70%); m.p. 229 – 231 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.66 (s, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.6 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.34 (s, 1H), 7.18 – 7.04 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 179.9, 145.8, 141.9, 136.8, 133.6, 132.3, 128.7, 128.0, 127.5, 126.2, 124.40, 124.38, 112.1, 112.0, 107.7; **HRMS (ESI)** m/z calcd. for $C_{15}H_7Cl_2NONa$ $[M+Na]^+$: 309.9802, found: 309.9797.

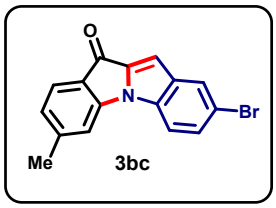
2-Bromo-10*H*-indolo[1,2-*a*]indol-10-one (3ac).[5]



3ac

Yellow solid (59.0 mg, 65%); m.p. 197 – 199 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.81 (d, *J* = 0.9 Hz, 1H), 7.67 (d, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 1H), 7.51 (dd, *J* = 8.8, 1.2 Hz, 1H), 7.42 (d, *J* = 8.7 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.07 (s, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 181.3, 145.1, 136.4, 135.7, 134.0, 132.6, 130.8, 129.1, 127.3, 125.3, 124.3, 114.9, 112.5, 111.3, 106.7.

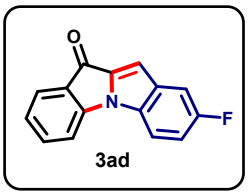
2-Bromo-7-methyl-10*H*-indolo[1,2-*a*]indol-10-one (3bc).



3bc

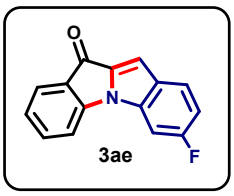
Yellow solid (64.0 mg, 68%); m.p. 208 – 210 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.79 (s, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 1H), 7.41 (d, *J* = 8.7 Hz, 1H), 7.14 (s, 1H), 7.03 (s, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 2.47 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 181.1, 147.4, 145.5, 136.9, 133.9, 132.5, 130.6, 127.2, 126.7, 125.1, 124.9, 114.7, 112.5, 112.1, 106.3, 22.5; **HRMS (ESI)** m/z calcd. for $C_{16}H_{10}BrNONa$ $[M+Na]^+$: 333.9843, found: 333.9837.

2-Fluoro-10*H*-indolo[1,2-*a*]indol-10-one (3ad).[4]



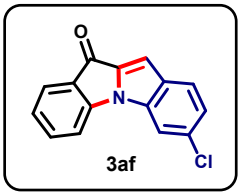
Yellow solid (51.0 mg, 71%); m.p. 244 – 246 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.66 (d, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.47 (dd, *J* = 8.9, 4.1 Hz, 1H), 7.37 – 7.28 (m, 2H), 7.19 (td, *J* = 9.0, 2.3 Hz, 1H), 7.14 – 7.04 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 181.5, 158.4 (d, $J_{C\text{-}F}$ = 239.8 Hz), 145.4, 137.0, 135.7, 133.0 (d, $J_{C\text{-}F}$ = 10.0 Hz), 130.9, 129.1, 125.4, 124.1, 116.8 (d, $J_{C\text{-}F}$ = 26.5 Hz), 112.1 (d, $J_{C\text{-}F}$ = 9.5 Hz), 111.0, 109.8 (d, $J_{C\text{-}F}$ = 23.6 Hz), 107.4 (d, $J_{C\text{-}F}$ = 4.9 Hz).

3-Fluoro-10*H*-indolo[1,2-*a*]indol-10-one (3ae).[4]



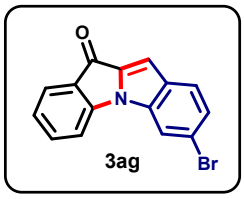
Yellow solid (55.0 mg, 78%); m.p. 242 – 244 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.67 (d, *J* = 7.0 Hz, 1H), 7.63 – 7.57 (m, 1H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 1H), 7.16 – 7.06 (m, 2H), 6.90 (t, *J* = 8.3 Hz, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 181.0, 163.4 (d, $J_{C\text{-}F}$ = 246.9 Hz), 145.1, 136.6 (d, $J_{C\text{-}F}$ = 3.3 Hz), 135.5, 134.3 (d, $J_{C\text{-}F}$ = 12.4 Hz), 129.5, 129.2, 126.2 (d, *J* = 10.7 Hz), 125.3, 124.3, 111.3, 111.1 (d, $J_{C\text{-}F}$ = 25.1 Hz), 107.9, 98.1 (d, *J* = 27.2 Hz).

3-Chloro-10*H*-indolo[1,2-*a*]indol-10-one (3af).[5]



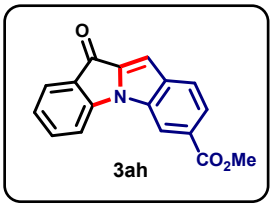
Yellow solid (56.0 mg, 73%); m.p. 197 – 199 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.66 (d, *J* = 7.4 Hz, 1H), 7.58 – 7.52 (m, 2H), 7.49 (s, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.17 – 7.05 (m, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 181.2, 145.0, 136.2, 135.6, 134.2, 134.1, 131.0, 129.2, 125.7, 125.3, 124.3, 122.8, 111.4, 111.3, 107.7.

3-Bromo-10*H*-indolo[1,2-*a*]indol-10-one (3ag).[5]



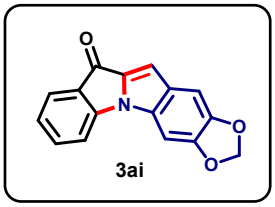
Yellow solid (64.0 mg, 71%); m.p. 195 – 197 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.70 (s, 1H), 7.68 (d, *J* = 7.5 Hz, 1H), 7.58 – 7.54 (m, 1H), 7.52 (d, *J* = 8.5 Hz, 1H), 7.37 (d, *J* = 7.9 Hz, 1H), 7.27 – 7.24 (m, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.10 (s, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 181.2, 144.9, 136.0, 135.6, 134.4, 131.3, 129.2, 125.9, 125.4, 125.3, 124.4, 122.1, 114.3, 111.4, 107.7.

Methyl 10-oxo-10*H*-indolo[1,2-*a*]indole-3-carboxylate (3ah).[6]



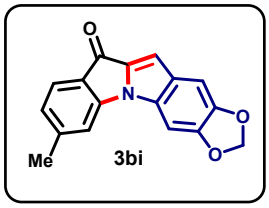
Yellow solid (29.0 mg, 35%); m.p. 210 – 212°C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.27 (s, 1H), 7.83 (d, *J* = 8.3 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 7.5 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.18 – 7.13 (m, 2H), 4.00 (s, 3H). 8.27 (s, 1H), 7.83 (d, *J* = 8.3 Hz, 1H), 7.71 (m, 2H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.20 – 7.11 (m, 2H), 4.00 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 181.6, 167.0, 145.3, 137.9, 135.95, 135.82, 133.5, 129.3, 129.0, 125.4, 124.7, 124.4, 122.6, 113.1, 111.8, 107.1, 52.5.

10*H*-[1,3]Dioxolo[4,5-*f*]indolo[1,2-*a*]indol-10-one (3ai).



Brick red solid (18.0 mg, 23%); m.p. 168 – 170 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.62 (d, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 1H), 7.08 (t, *J* = 7.3 Hz, 1H), 7.03 – 6.90 (m, 3H), 6.02 (s, 2H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 180.5, 150.0, 144.9, 144.5, 134.98, 134.87, 130.6, 129.8, 126.8, 124.9, 123.9, 110.7, 108.6, 102.3, 101.6, 91.9; **HRMS (ESI)** m/z calcd. for $C_{16}H_{10}NO_3$ $[M+H]^+$: 264.0661, found: 264.0653.

7-Methyl-10*H*-[1,3]dioxolo[4,5-*f*]indolo[1,2-*a*]indol-10-one (3bi).



Brick red solid (22.0 mg, 26%); m.p. 194 – 197 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.50 (d, *J* = 7.0 Hz, 1H), 7.04 (s, 1H), 7.03 – 6.91 (m, 3H), 6.87 (d, *J* = 6.9 Hz, 1H), 6.01 (s, 2H), 2.44 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 180.5, 149.8, 146.5, 145.4, 144.4, 135.5, 130.5, 127.5, 126.8, 124.8, 124.6, 111.6, 108.2, 102.3, 101.6, 92.0, 22.5; **HRMS (ESI)** m/z calcd. for $C_{17}H_{11}NO_3Na$ $[M+Na]^+$: 300.0637, found: 300.0631.

7. References

(1) Vaitla, J.; Bayer, A.; Hopmann, K. H. *Angew. Chem., Int. Ed.* **2017**, 56, 4277.

(2) Chauhan, J.; Fletcher, S. *Tetrahedron Lett.* **2012**, 53, 4951.

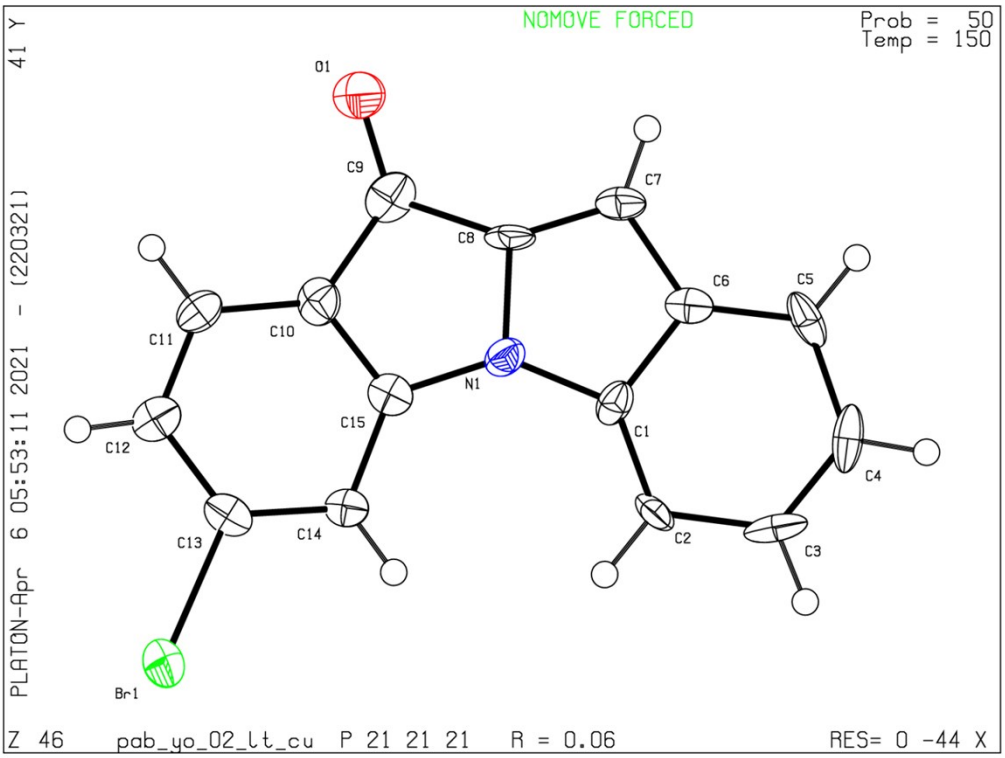
(3) Wu, X.; Xiao, Y.; Sun, S.; Yu, J.-T.; Cheng, J. *Org. Lett.* **2019**, *21*, 6653.

(4) Liu, M.; Liu, Y.-W.; Xu, H.; Dai, H.-X. *Tetrahedron Lett.* **2019**, *60*, 151061.

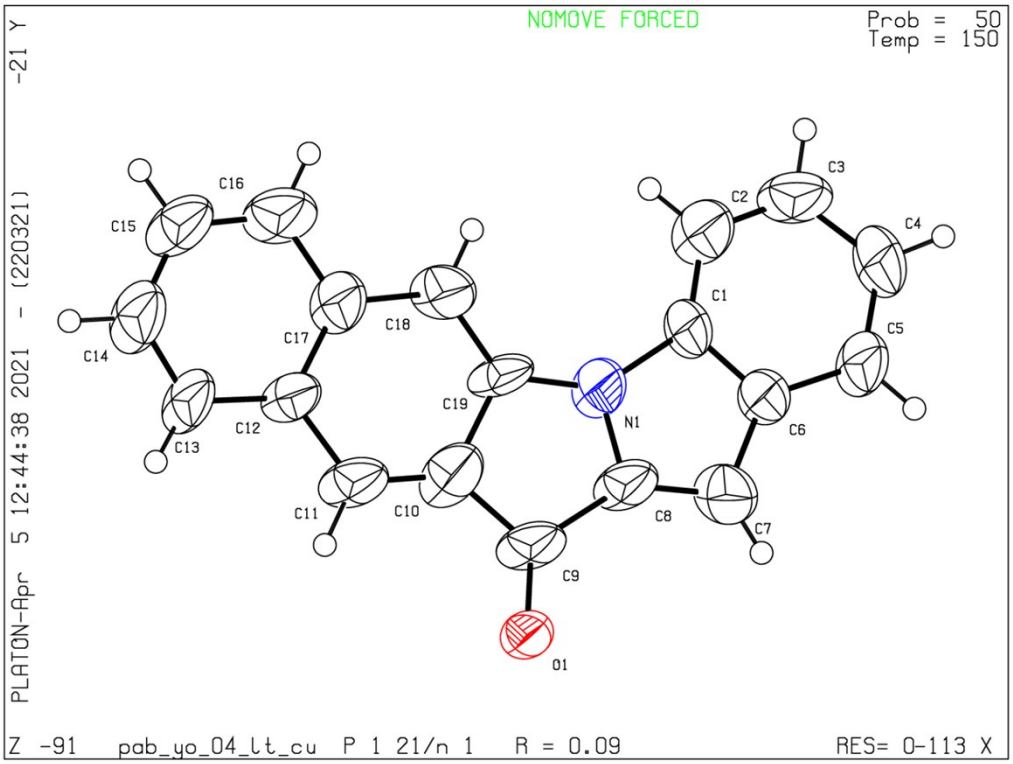
(5) Zou, S.; Liu, Y.; Xi, C. *ACS Omega* **2019**, *4*, 18734.

8. X-ray Structures

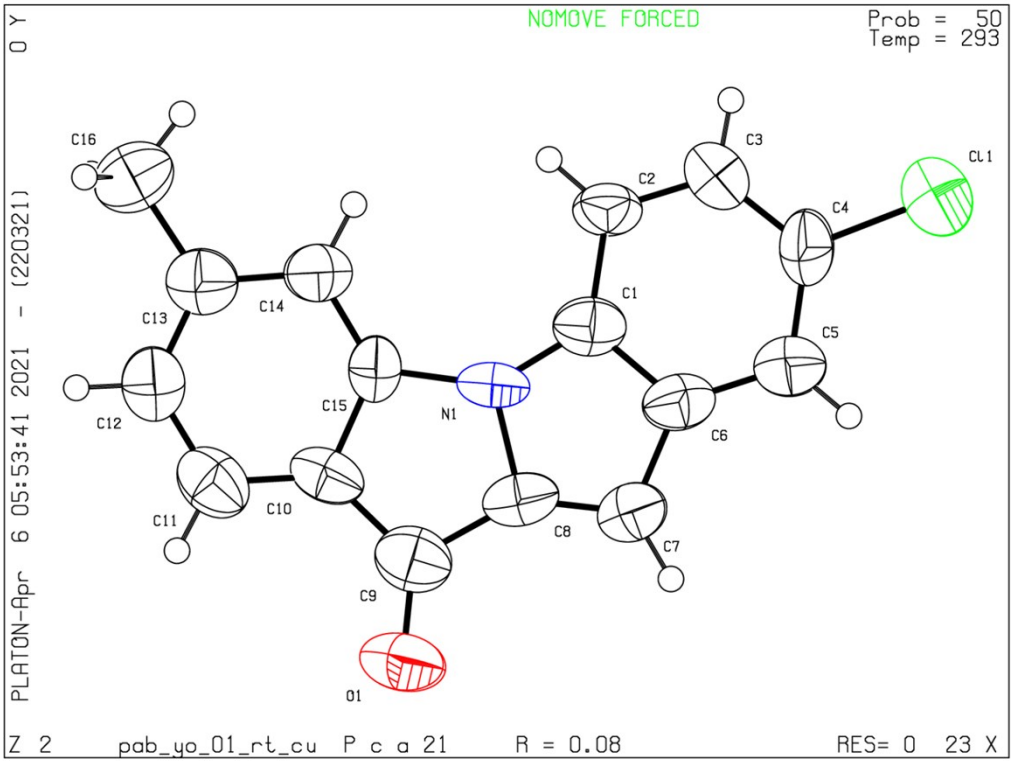
(a) X-ray Structure of **3ha** with 50% ellipsoid probability



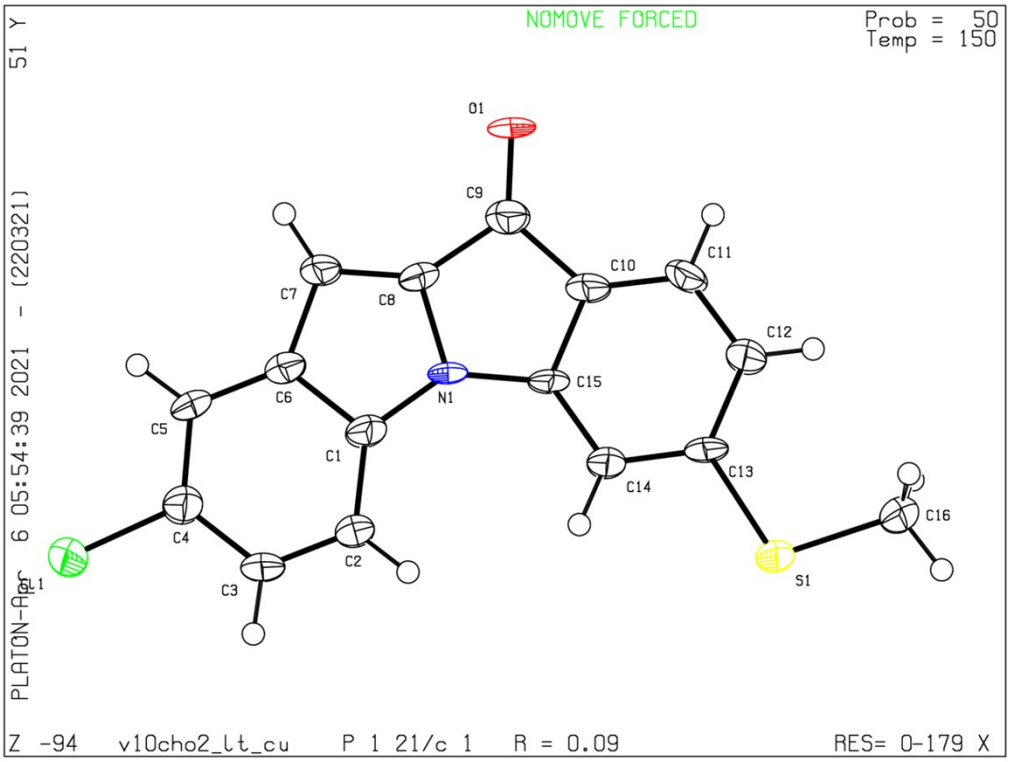
(b) X-ray Structure of **3pa** with 50% ellipsoid probability



(c) X-ray Structure of **3bb** with 50% ellipsoid probability

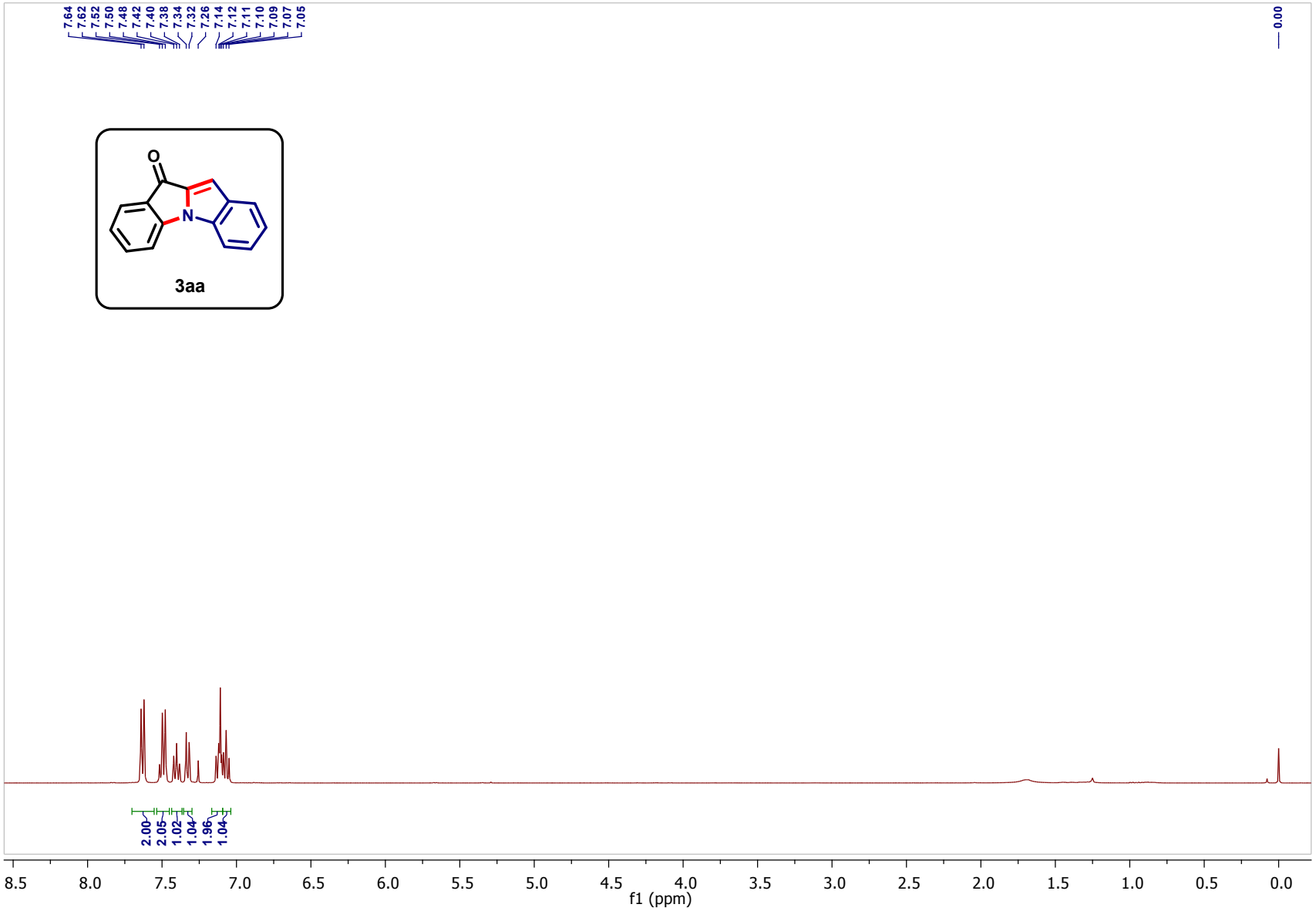


(c) X-ray Structure of **3fb** with 50% ellipsoid probability



Appendix I

Spectral Copies of ^{1}H and ^{13}C NMR of Compounds Obtained in this Study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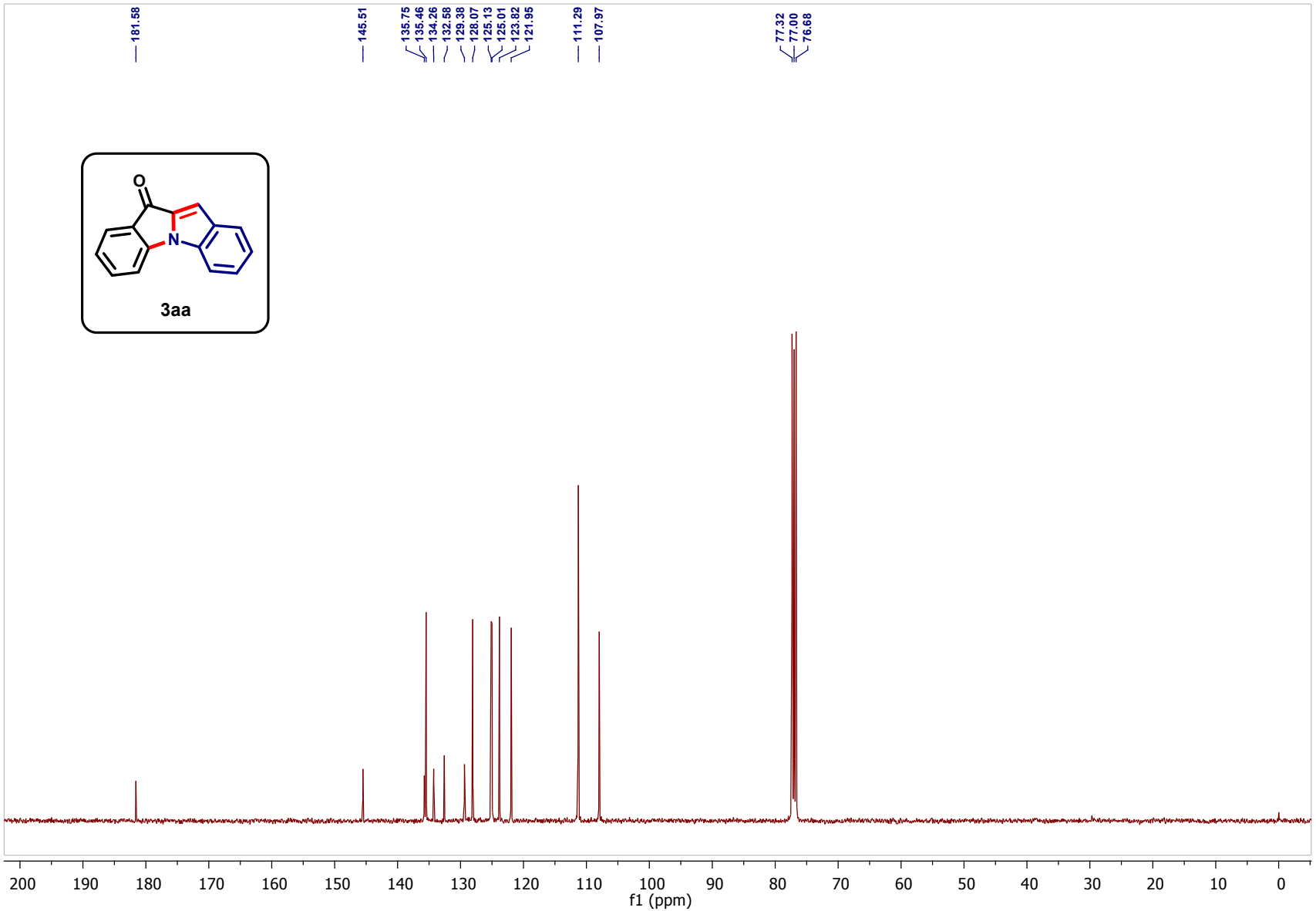
7.52
7.50
7.48
7.42
7.40
7.38
7.34
7.32
7.26
7.14
7.12
7.11
7.10
7.09
7.07
7.05
0.00
O
N
3aa
2.00
2.05
1.02
1.04
1.96
1.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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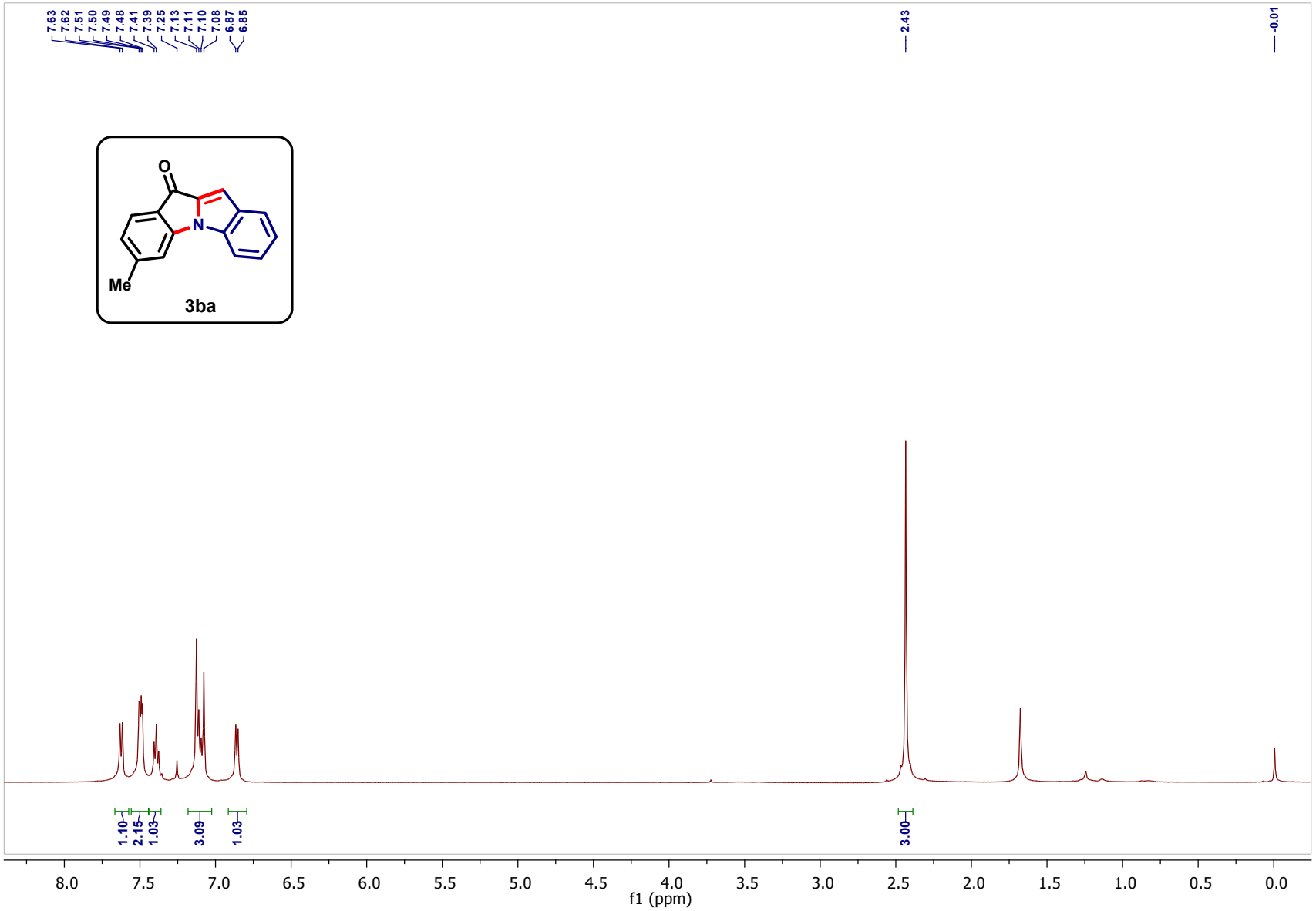
145.51
135.75
135.46
134.26
132.58
129.38
128.07
125.13
125.01
123.82
121.95
111.29
107.97
77.32
77.00
76.68
O
N
3aa
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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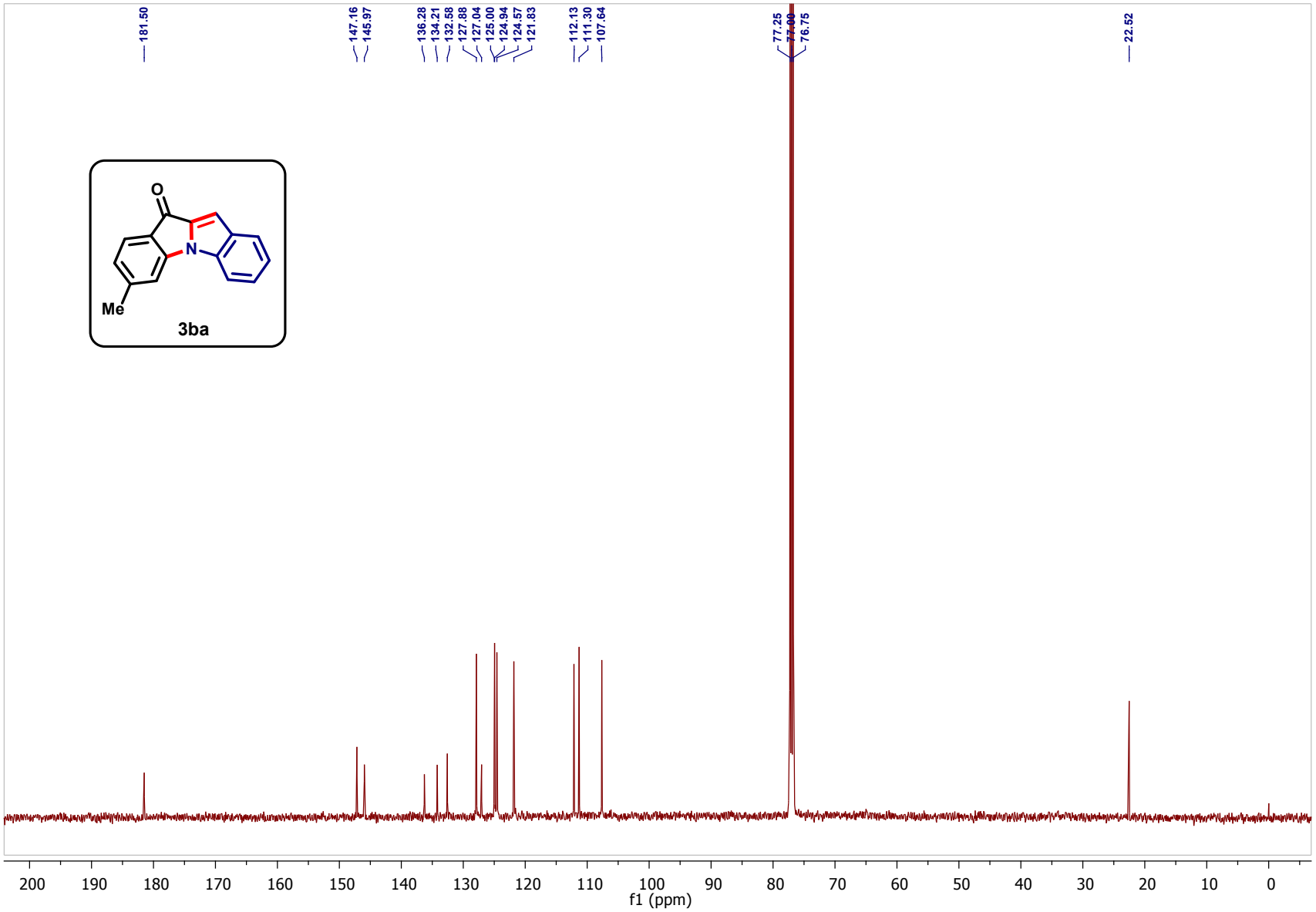
7.10
7.08
6.87
6.85
2.43
-0.01
O
N
Me
3ba
1.10
2.15
1.03
3.09
1.03
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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132.58
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127.04
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124.94
124.57
121.83
112.13
111.30
107.64
77.25
77.00
76.75
22.52
O
N
Me
3ba
200
190
180
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150
140
130
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110
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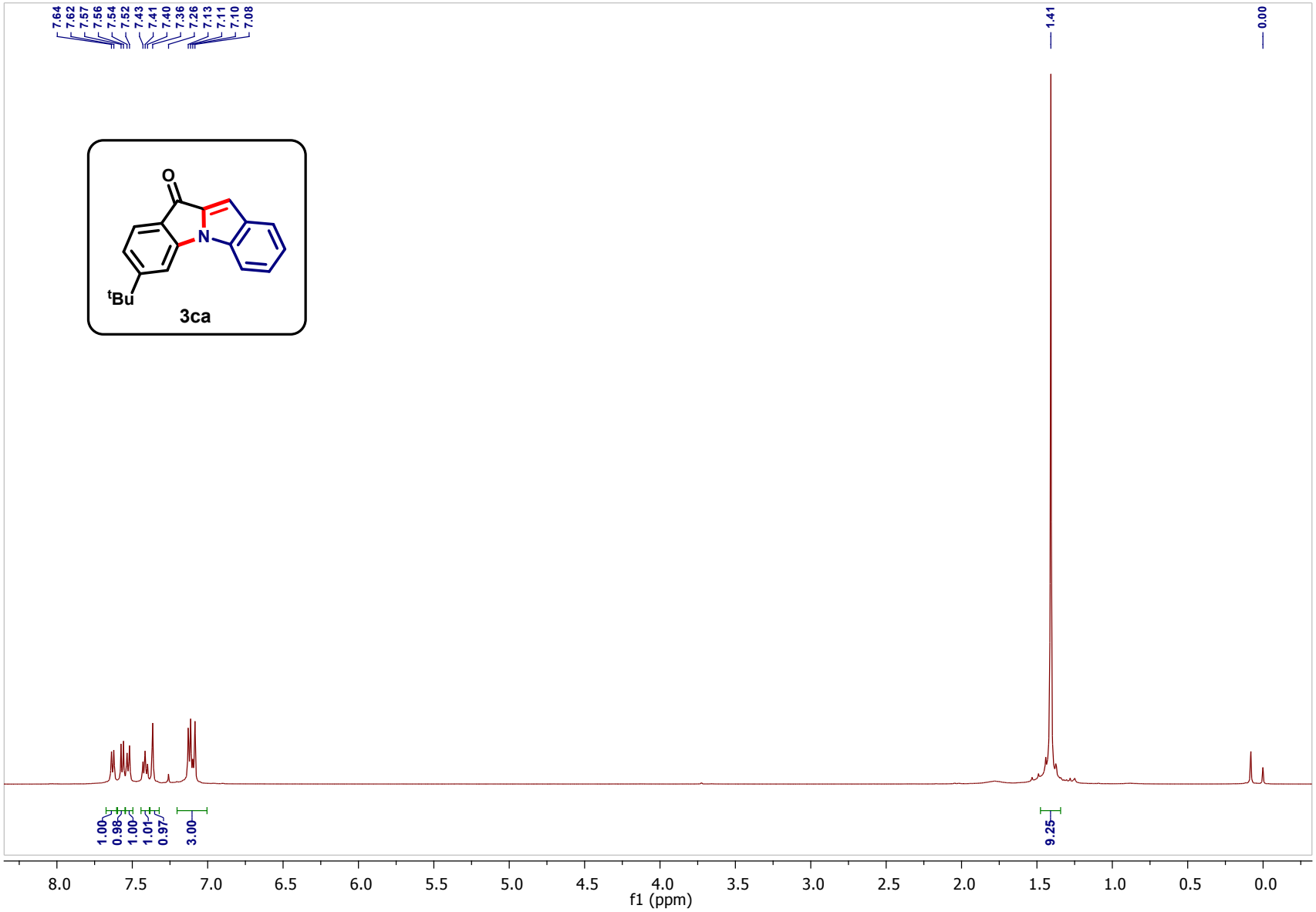
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.13
7.11
7.10
7.08
1.41
0.00
O
N
tBu
3ca
1.00
0.98
1.00
1.01
0.97
3.00
9.25
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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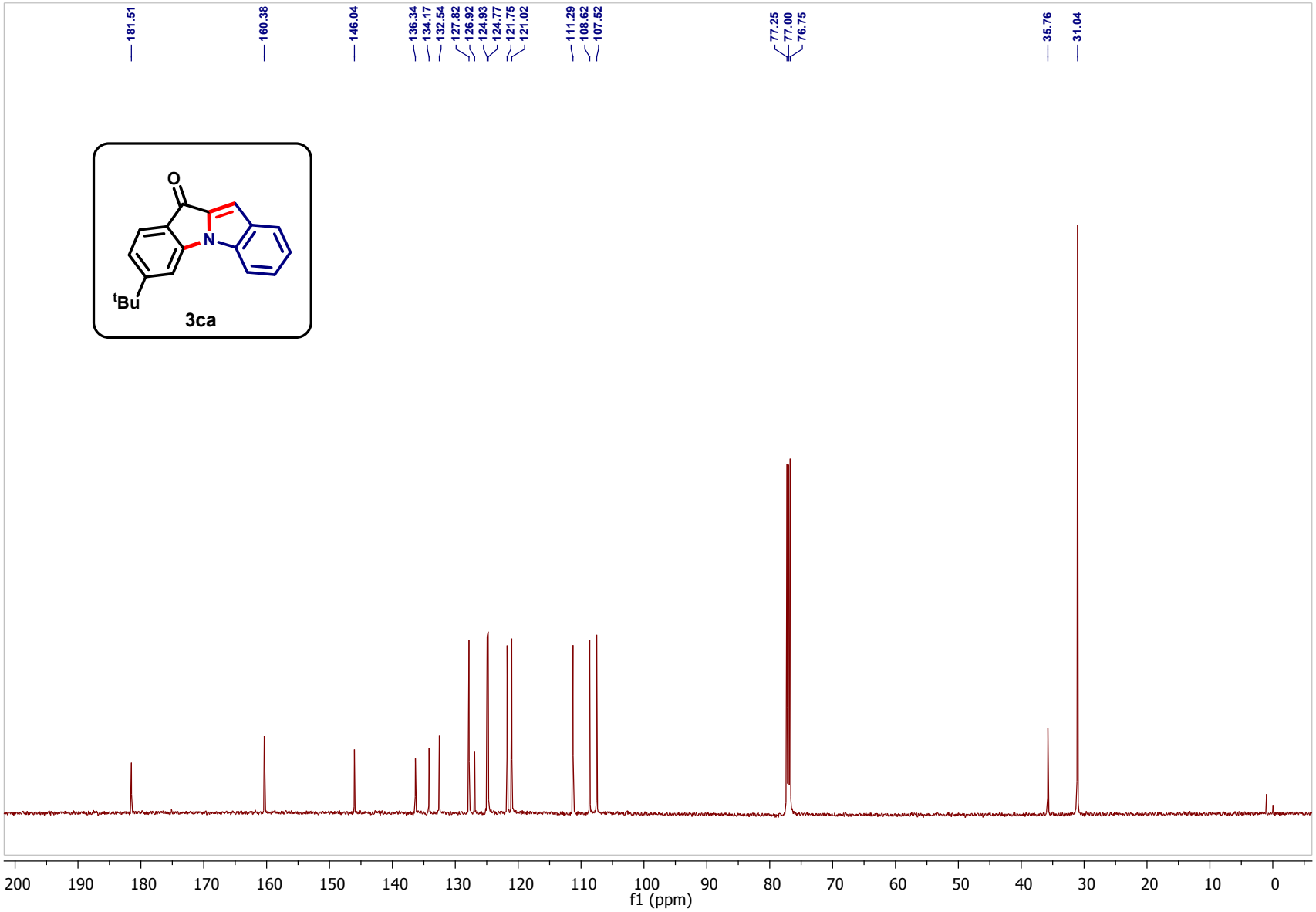
1.0
0.5
0.0
f1 (ppm)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121.75
121.02
111.29
108.62
107.52
77.25
77.00
76.75
35.76
31.04
O
N
tBu
3ca
200
190
180
170
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150
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130
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50
40
30
20
10
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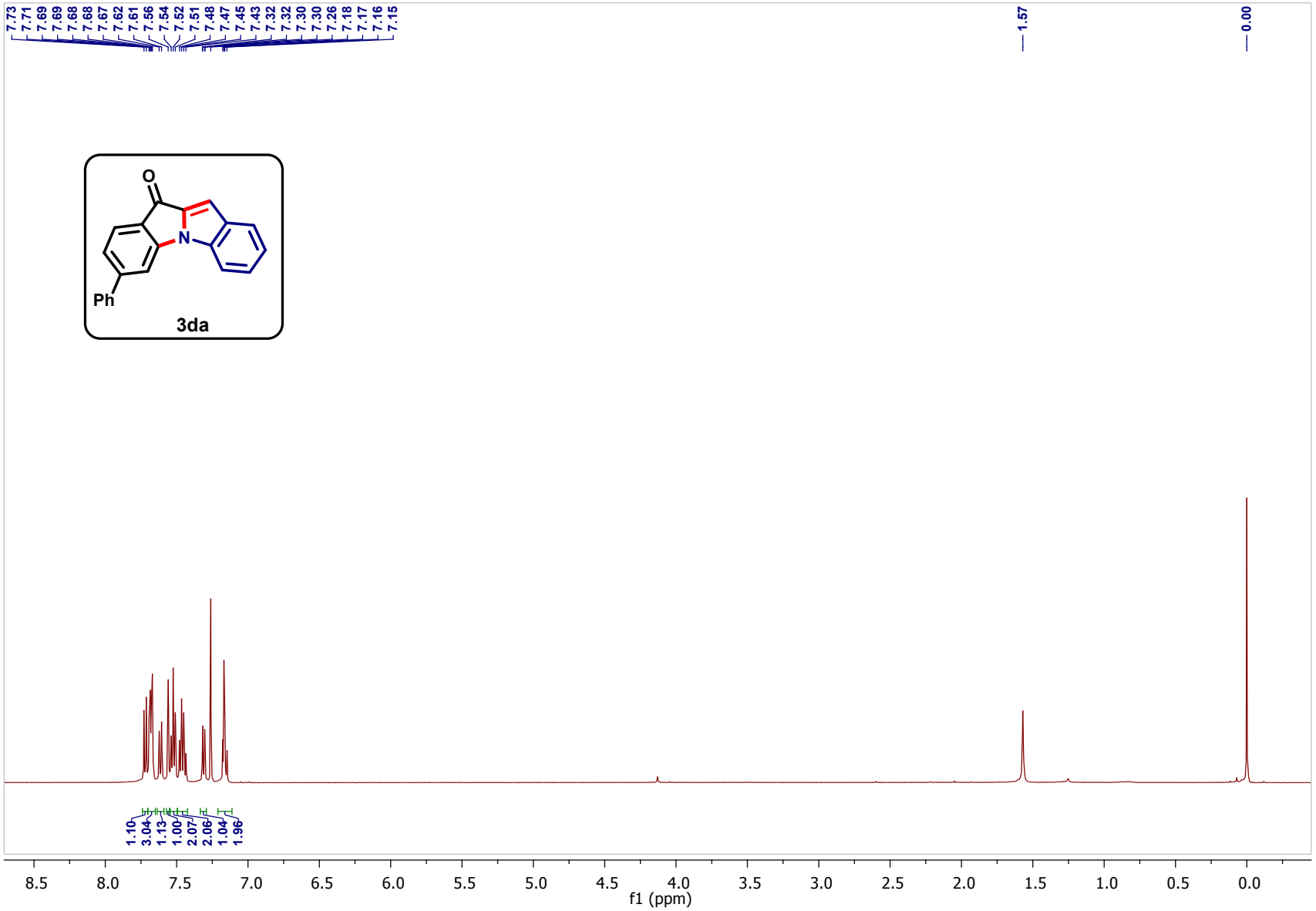
f1 (ppm)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7.45
7.43
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7.26
7.18
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7.16
7.15
1.57
0.00
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N
Ph
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3.04
1.13
1.00
2.07
2.06
1.04
1.96
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6.0
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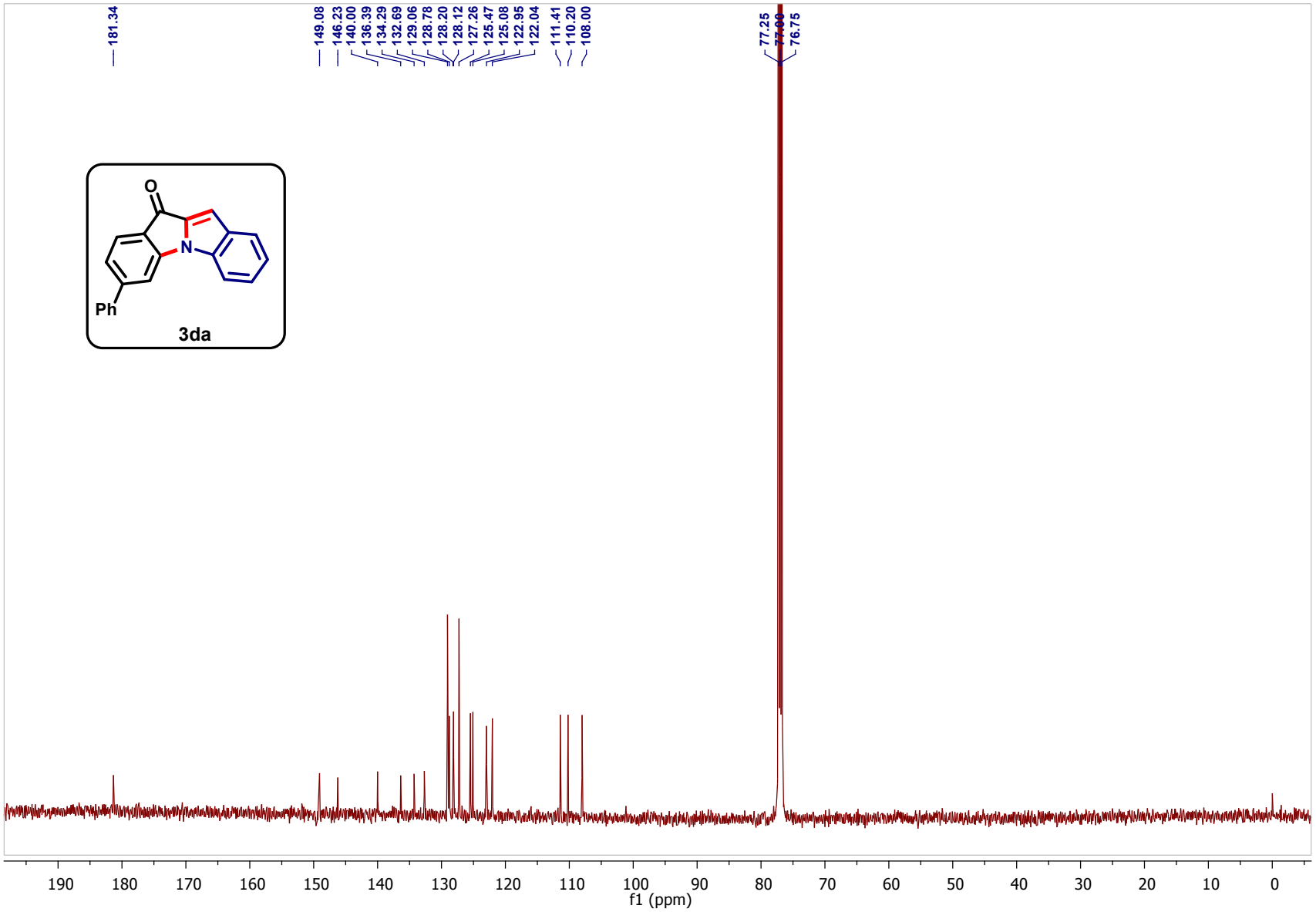
f1 (ppm)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111.41
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108.00
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76.75
O
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Ph
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110
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50
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30
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10
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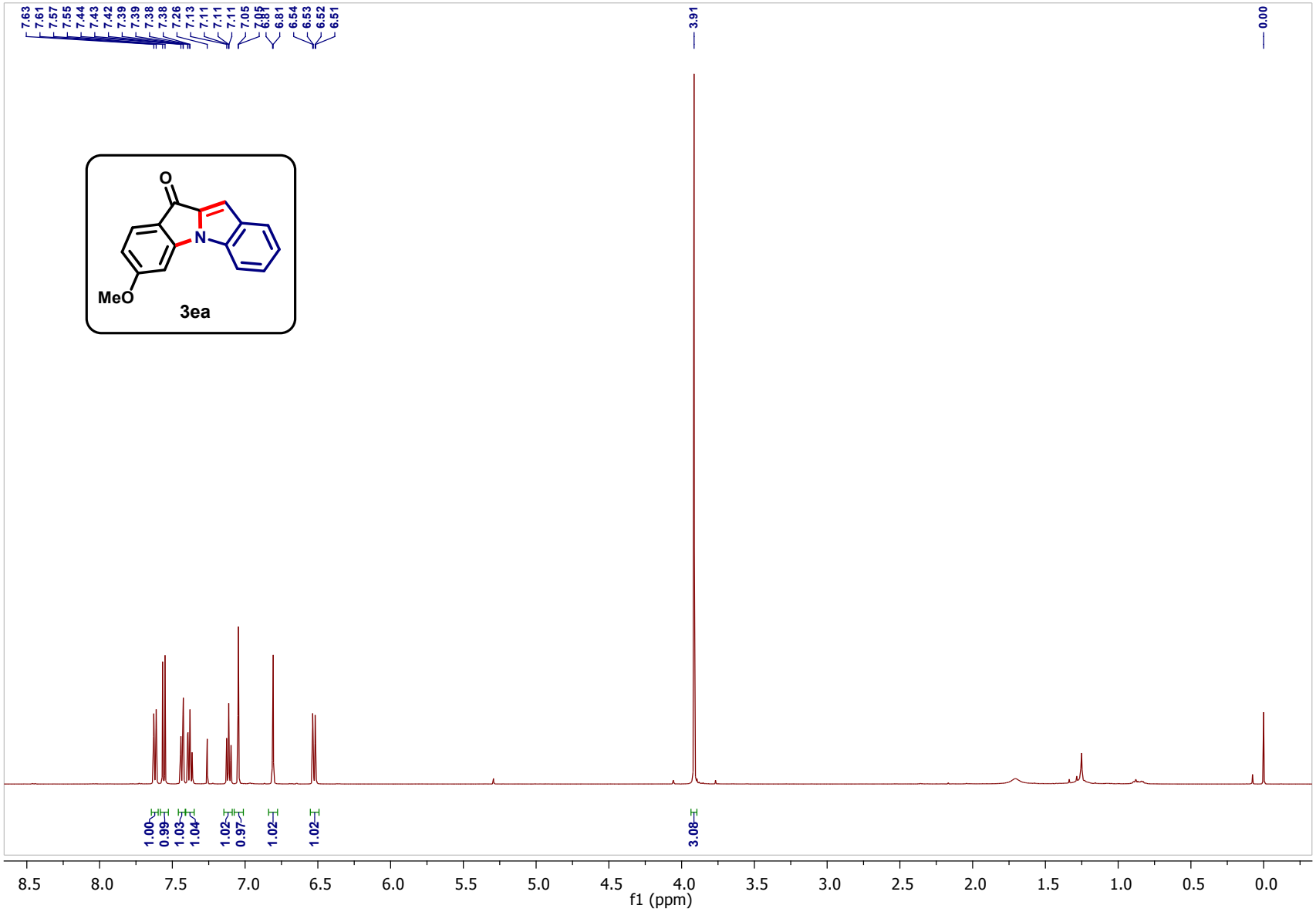
f1 (ppm)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6.81
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6.51
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0.97
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1.02
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6.0
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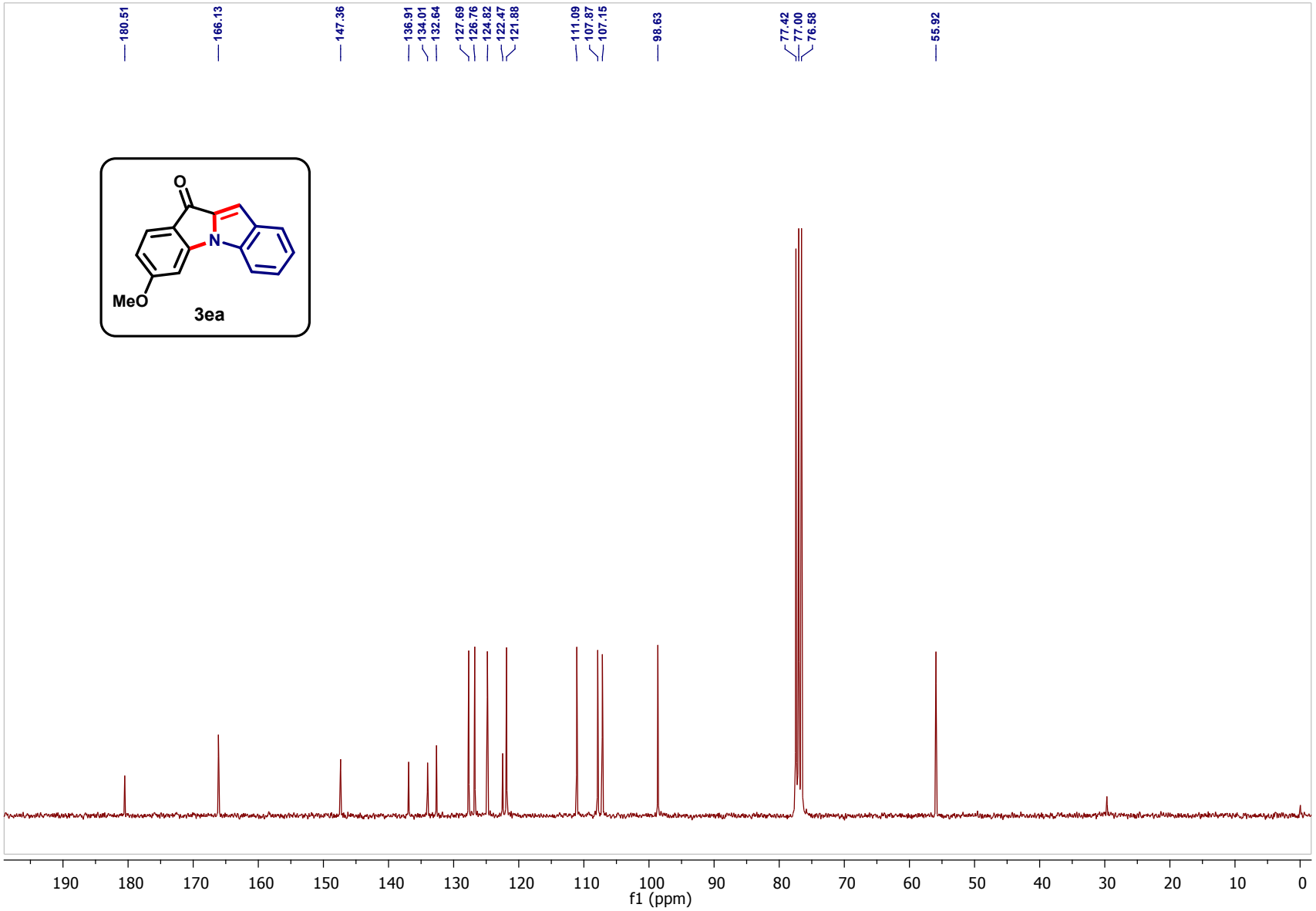
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107.15
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76.58
55.92
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MeO
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90
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70
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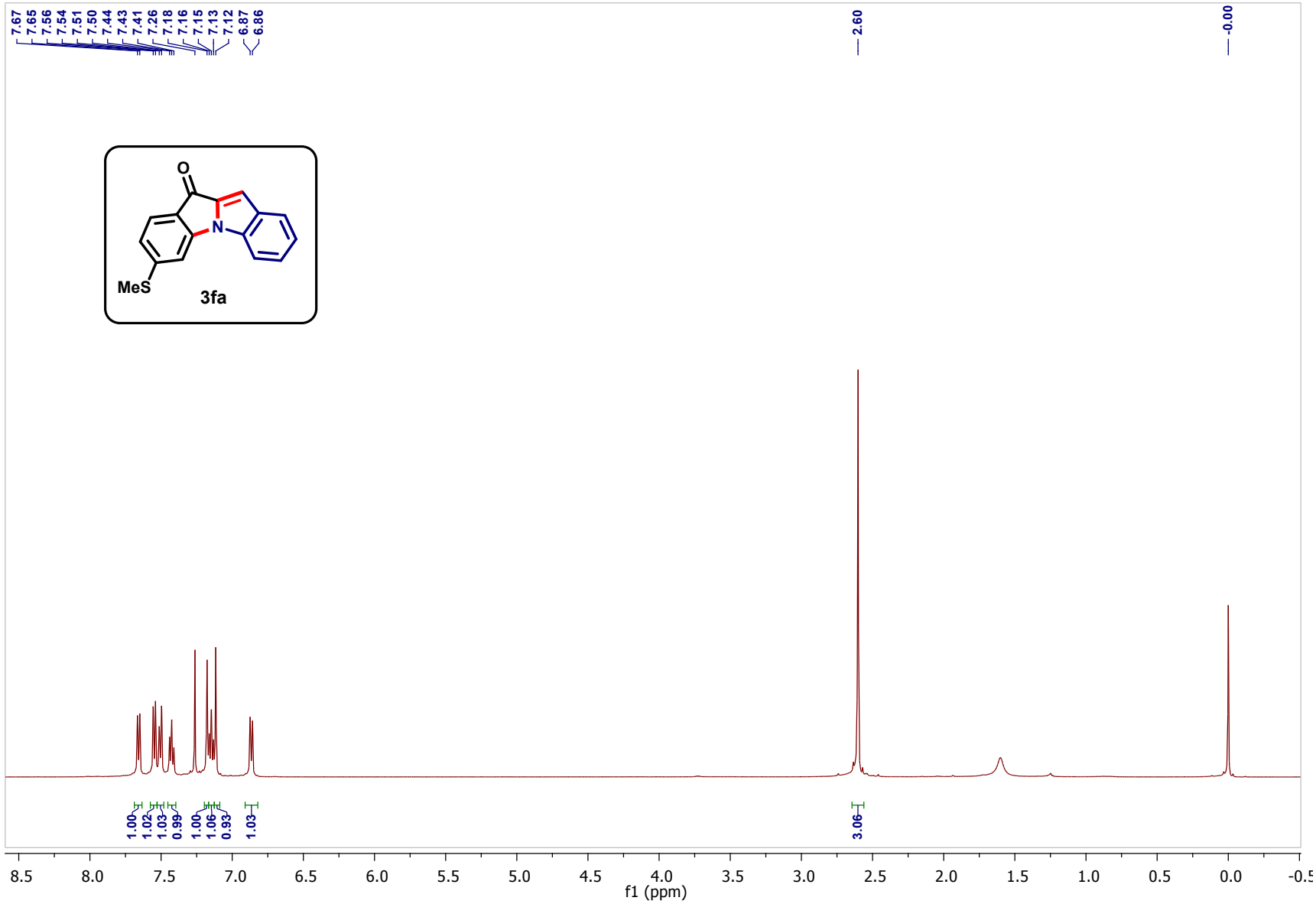
30
20
10
0
f1 (ppm)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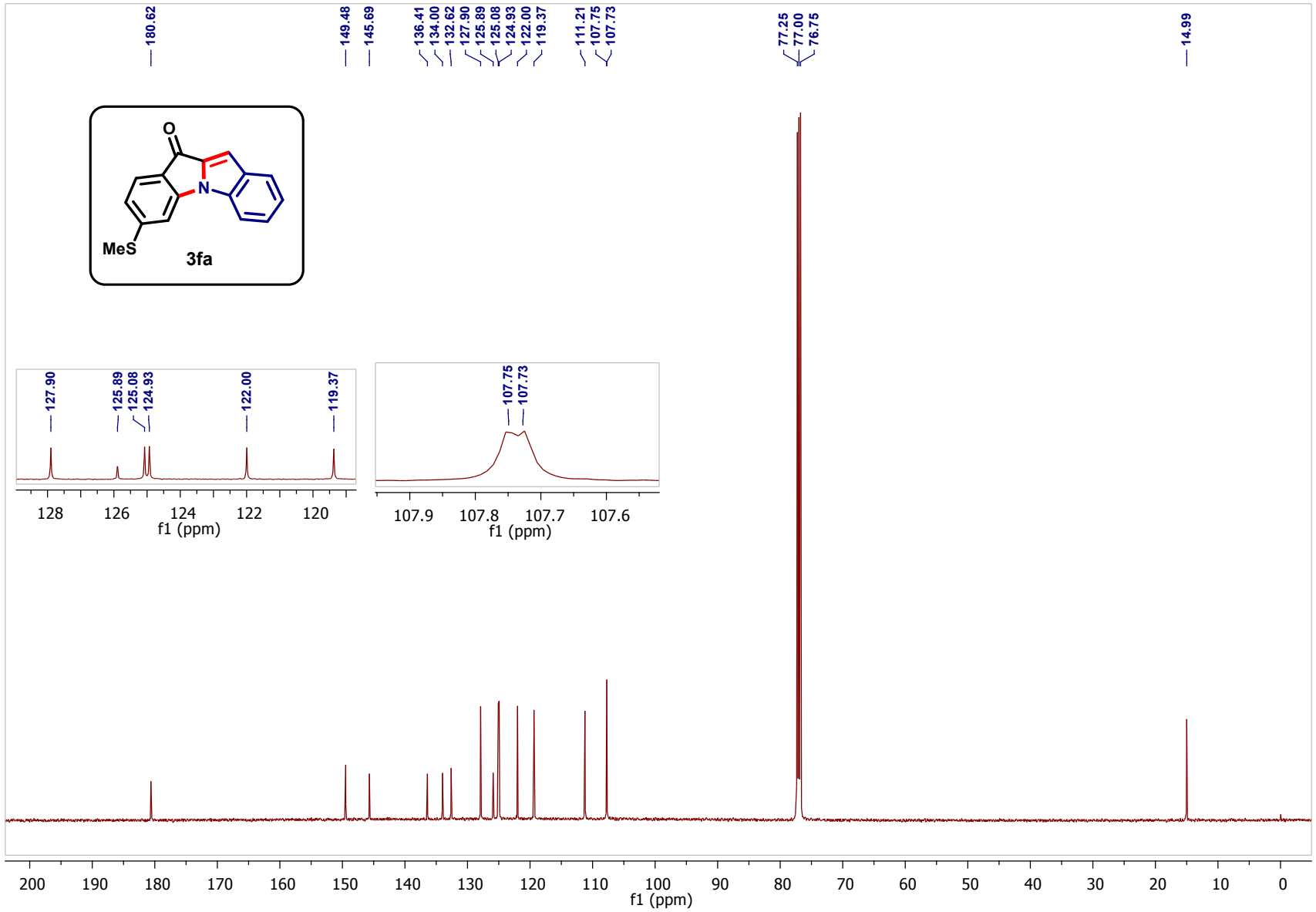
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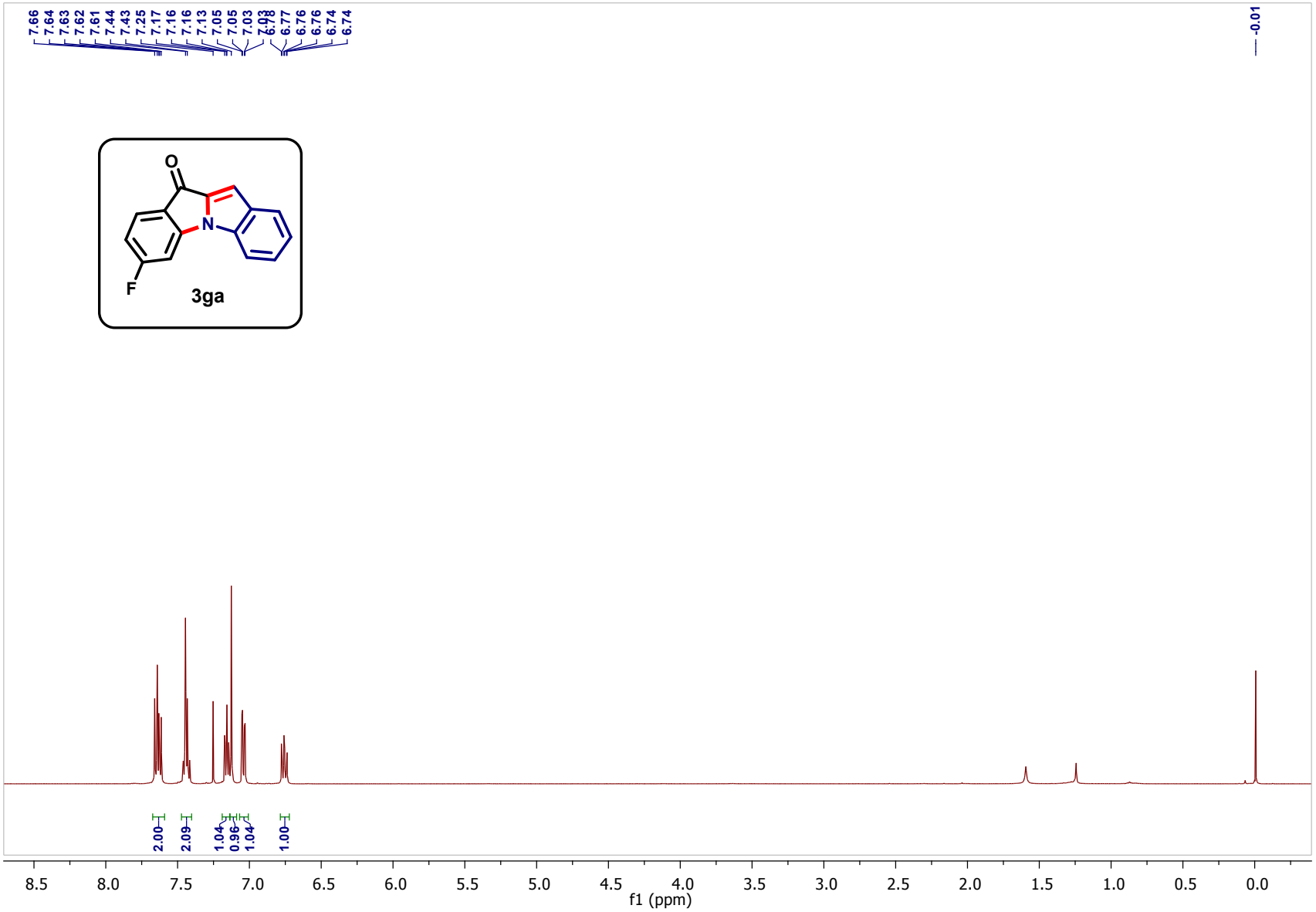
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1.04
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1.00
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8.0
7.5
7.0
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6.0
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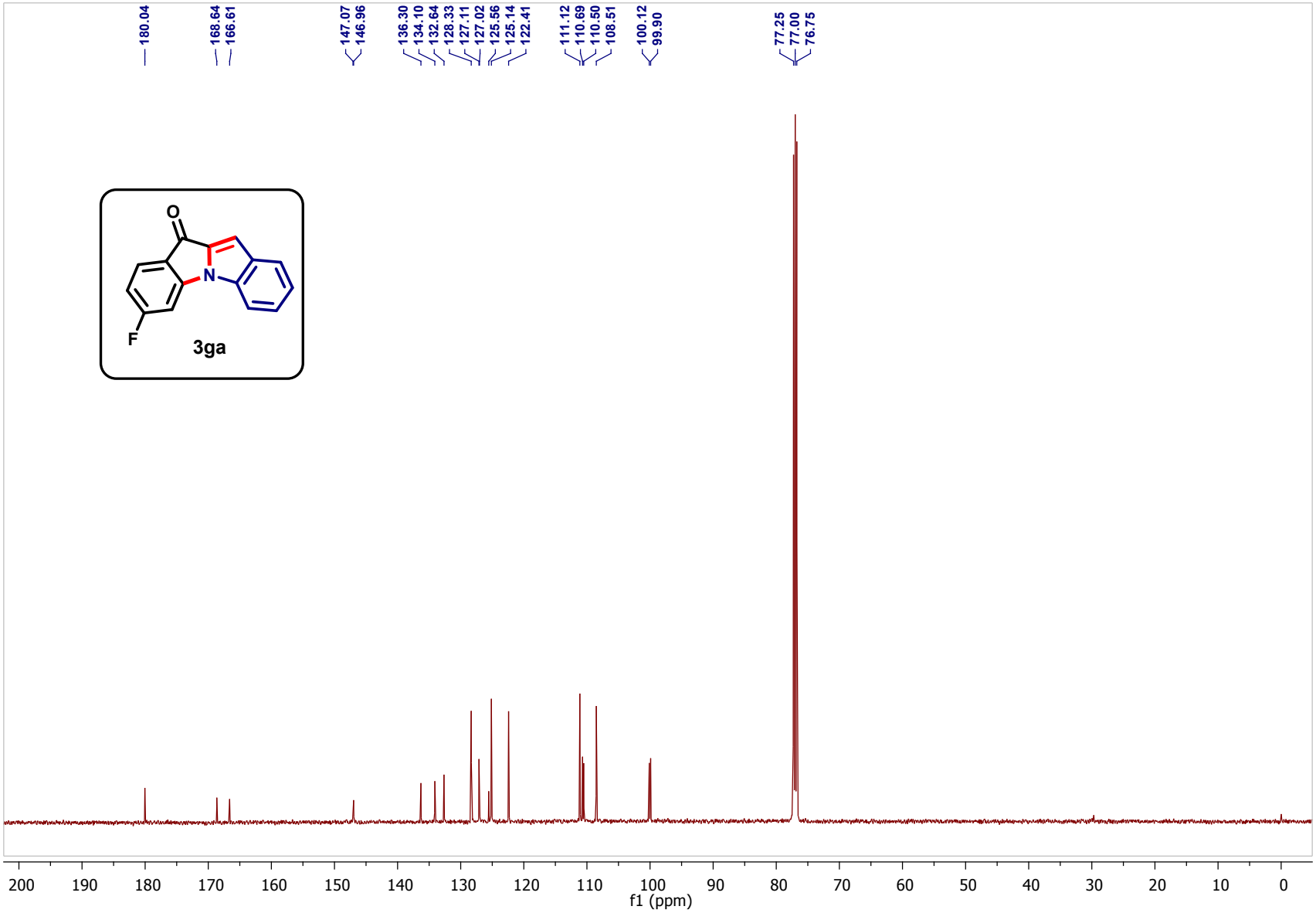
f1 (ppm)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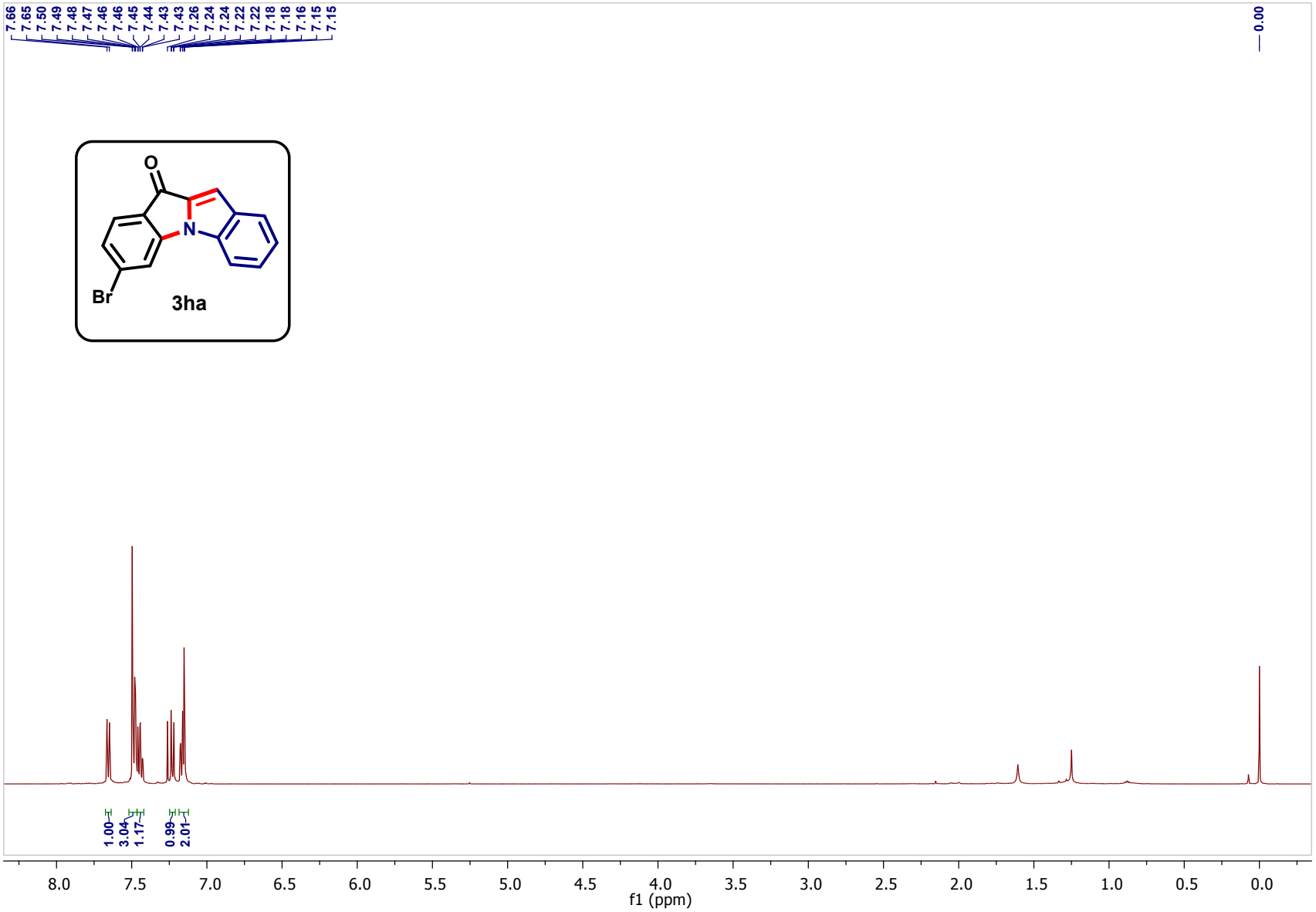
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7.0
6.5
6.0
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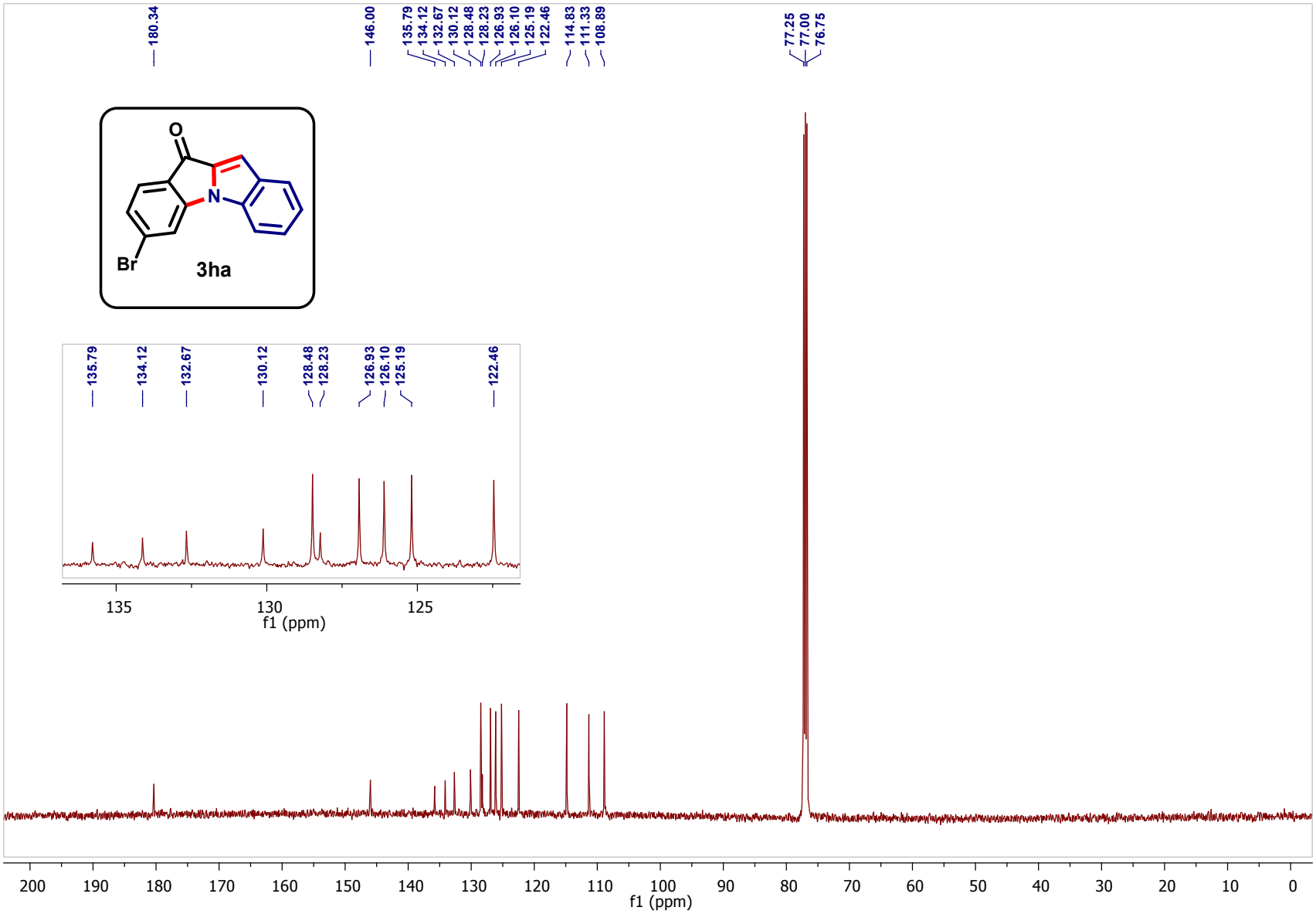
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200
190
180
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50
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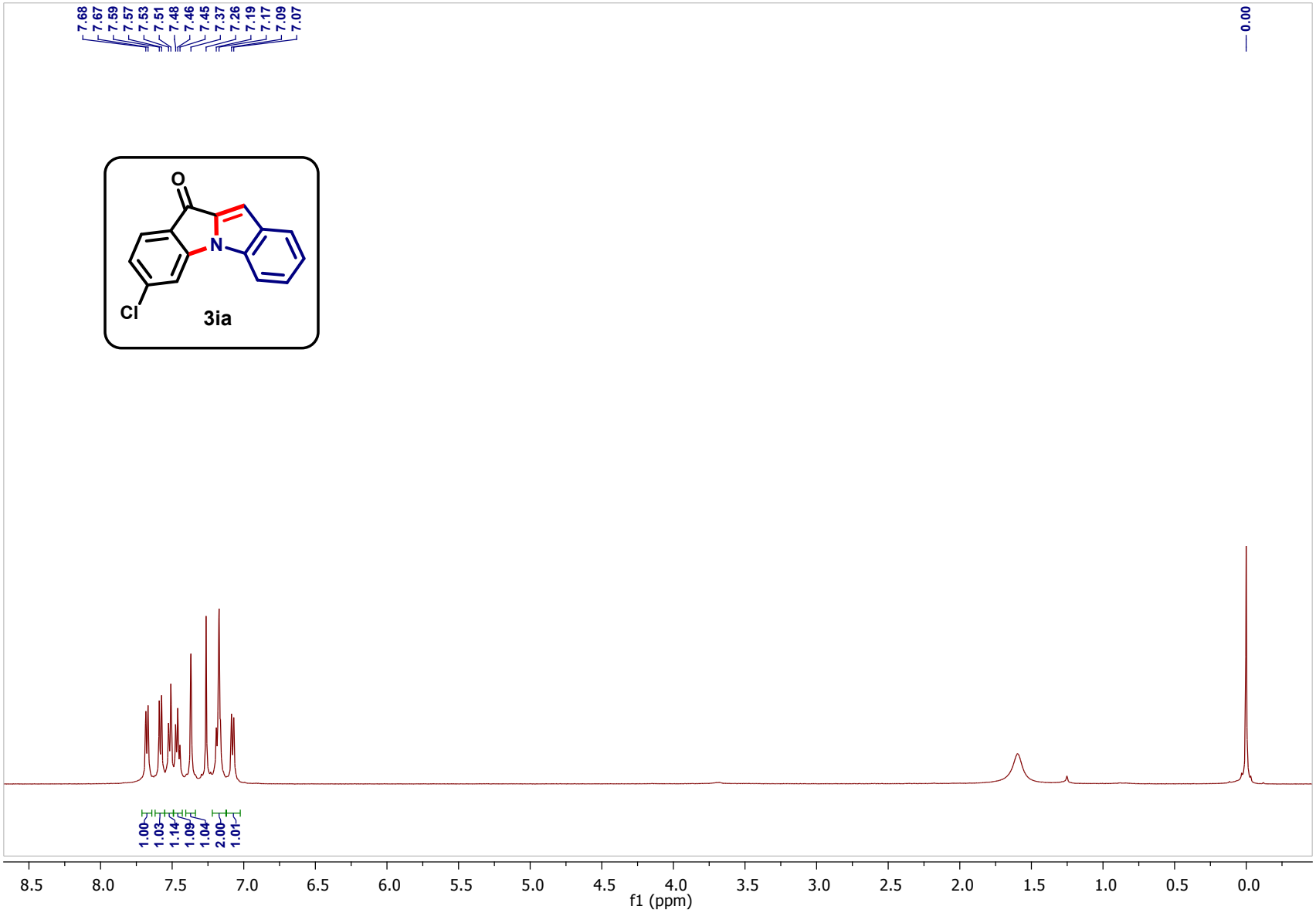
0
f1 (ppm)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7.45
7.37
7.26
7.19
7.17
7.09
7.07
0.00
O
N
Cl
3ia
1.00
1.03
1.14
1.09
1.04
2.00
1.01
8.5
8.0
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7.0
6.5
6.0
5.5
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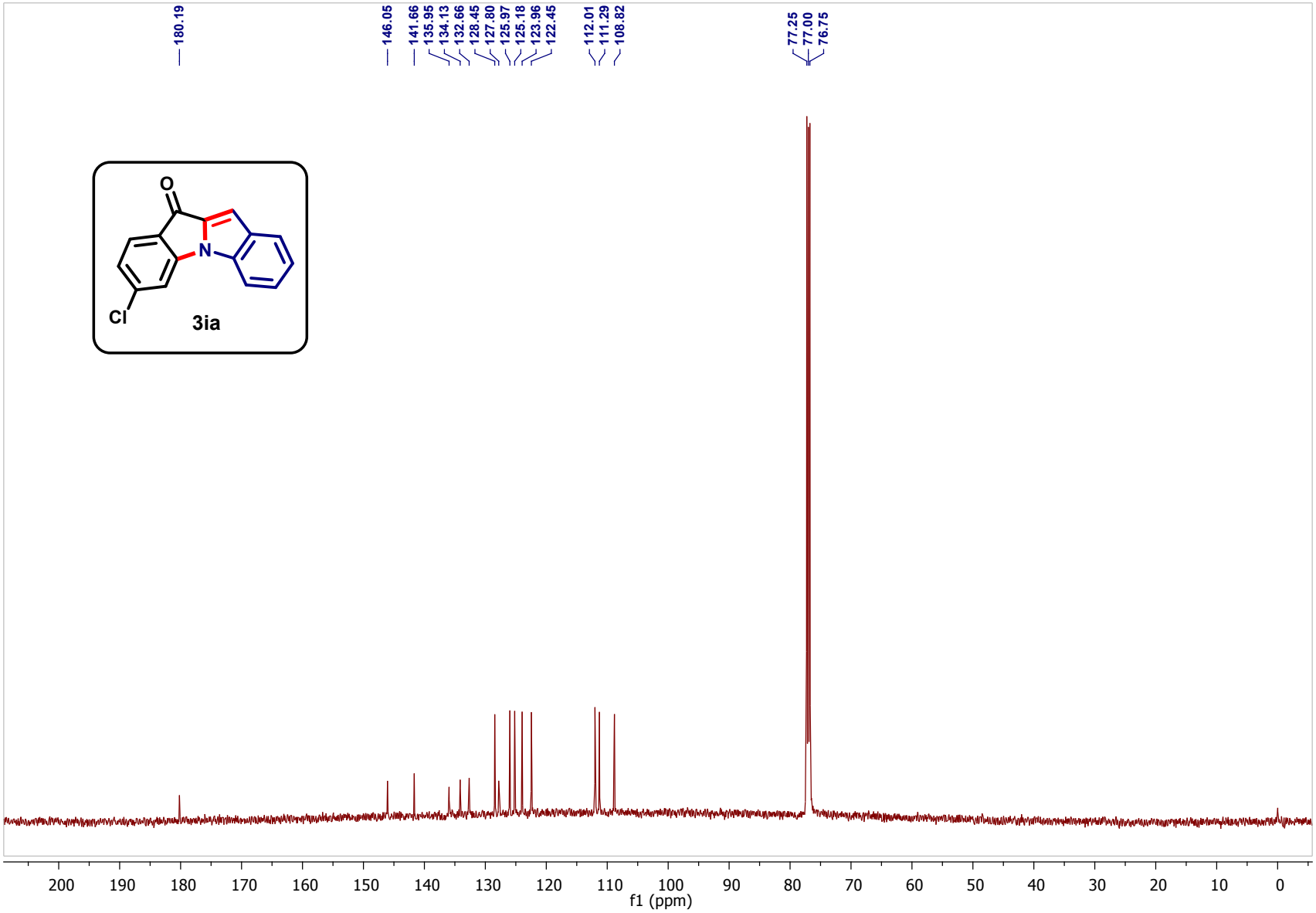
f1 (ppm)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125.18
123.96
122.45
112.01
111.29
108.82
77.25
77.00
76.75
O
N
Cl
3ia
200
190
180
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130
120
110
100
90
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70
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50
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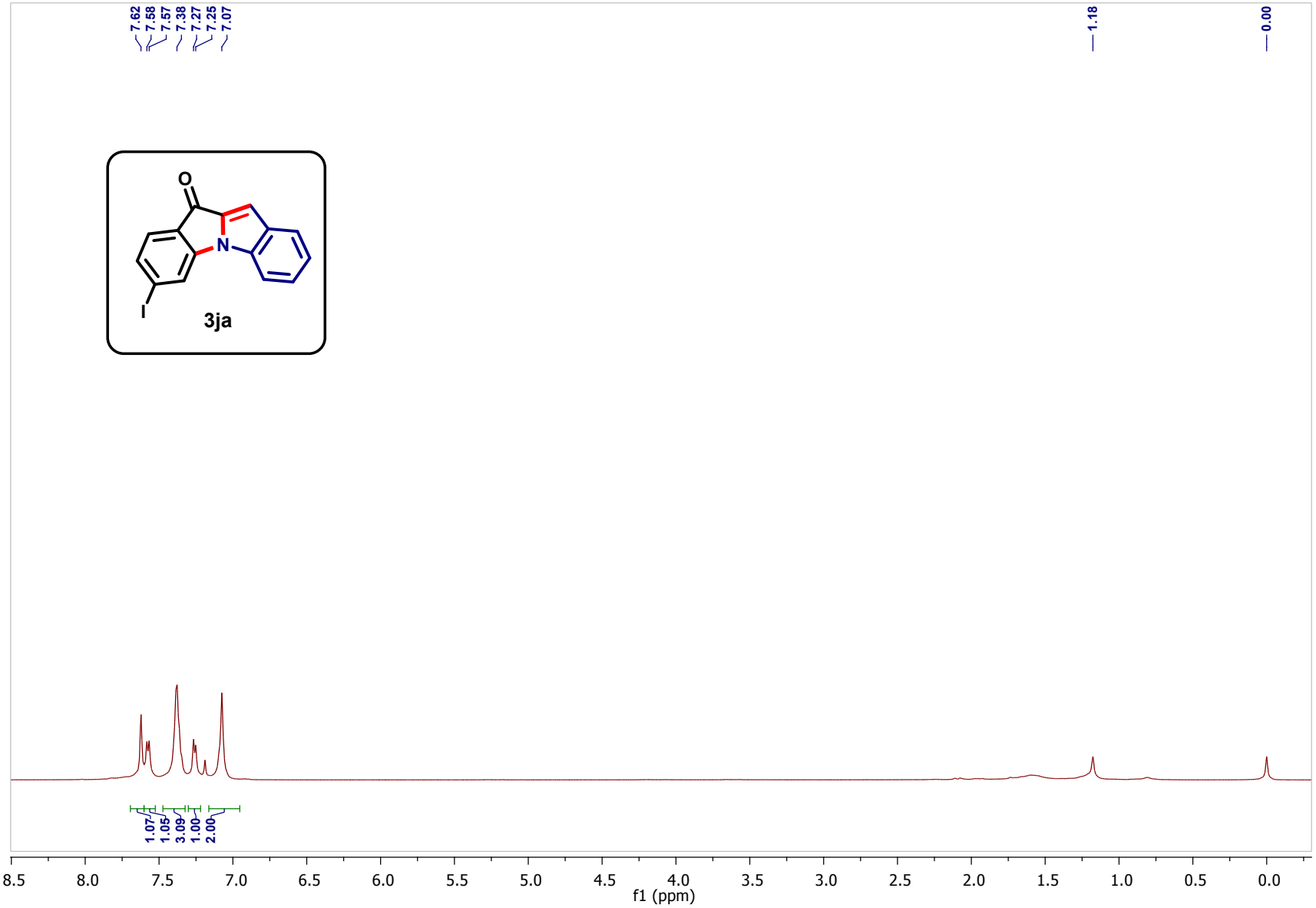
f1 (ppm)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N
I
3ja
1.07
1.05
3.09
1.00
2.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
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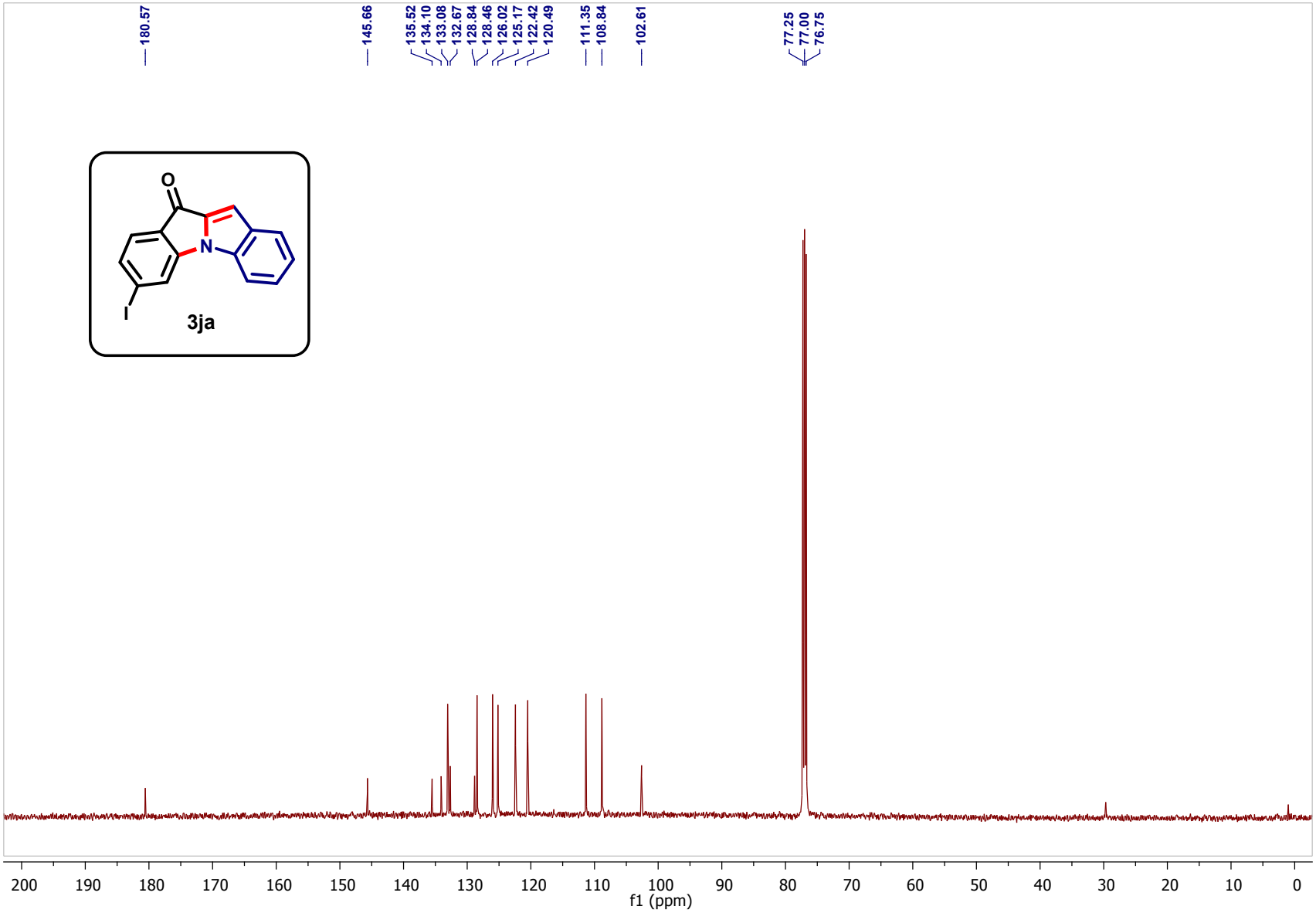
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128.46
126.02
125.17
122.42
120.49
111.35
108.84
102.61
77.25
77.00
76.75
O
N
I
3ja
200
190
180
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150
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130
120
110
100
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50
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10
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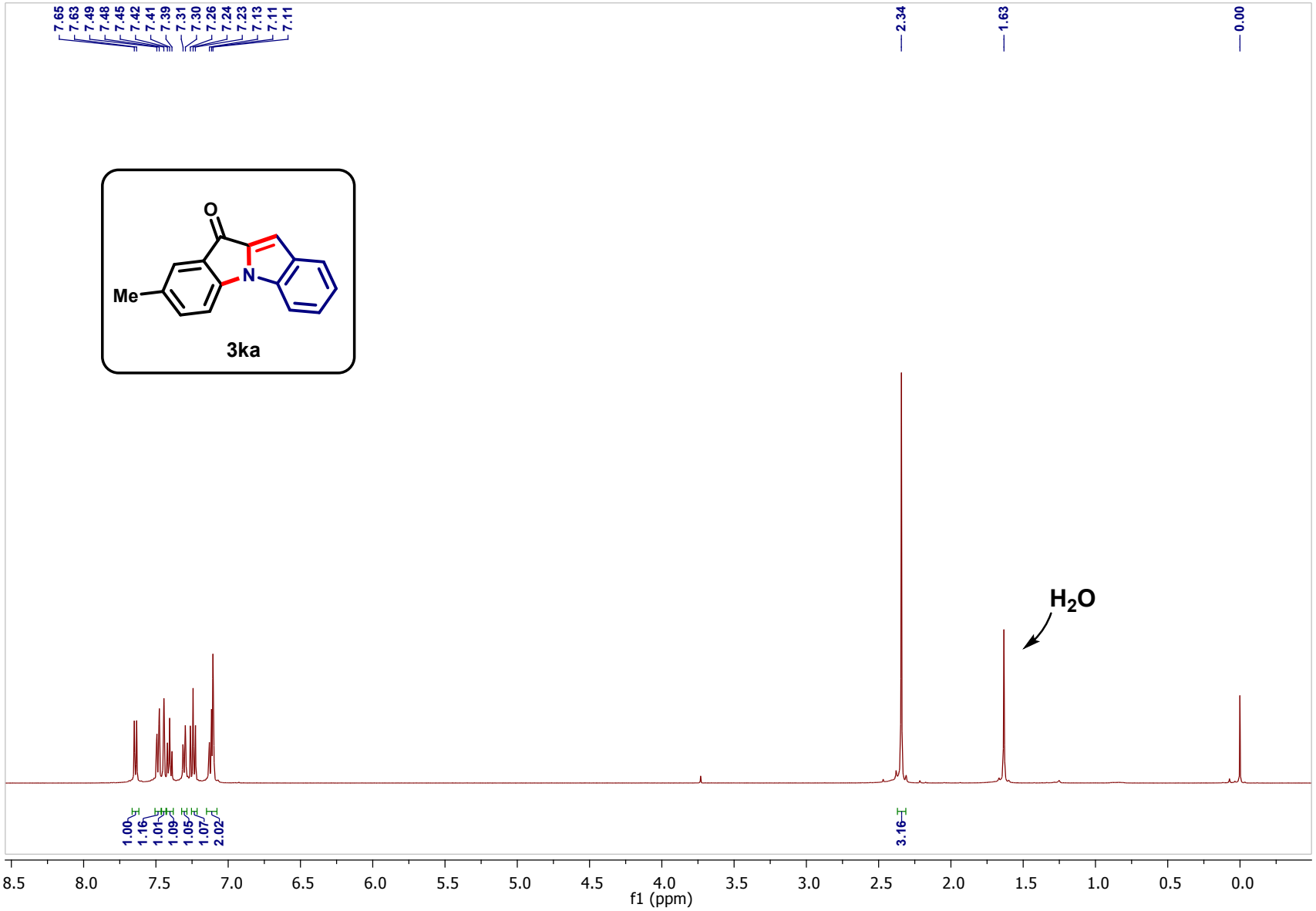
f1 (ppm)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7.39
7.31
7.30
7.26
7.24
7.23
7.13
7.11
7.11
2.34
1.63
0.00
O
N
Me
3ka
H2O
1.00
1.16
1.01
1.09
1.05
1.07
2.02
3.16
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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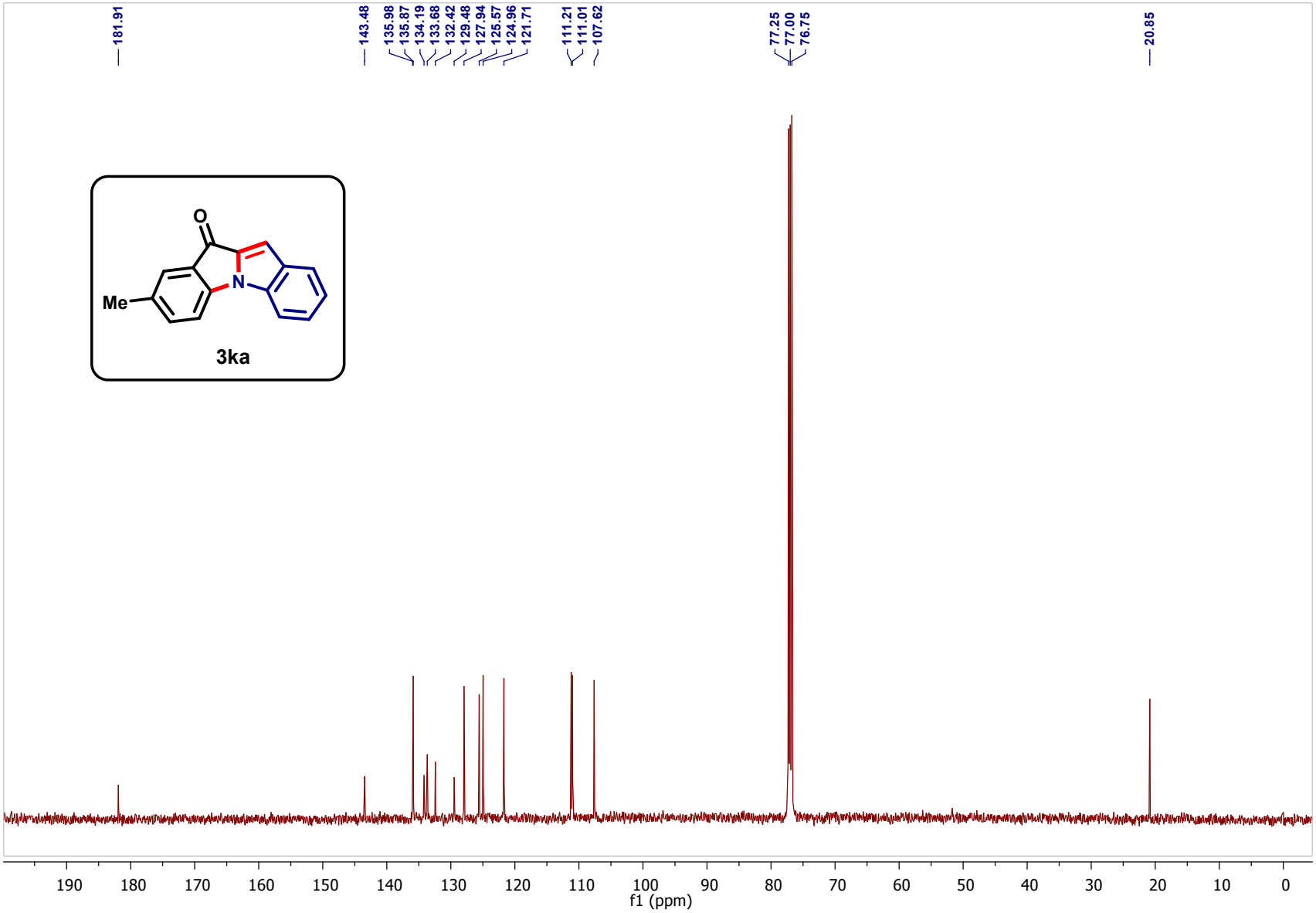
0.0
f1 (ppm)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135.87
134.19
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132.42
129.48
127.94
125.57
124.96
121.71
111.21
111.01
107.62
77.25
77.00
76.75
20.85
O
N
Me
3ka
190
180
170
160
150
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130
120
110
100
90
80
70
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50
40
30
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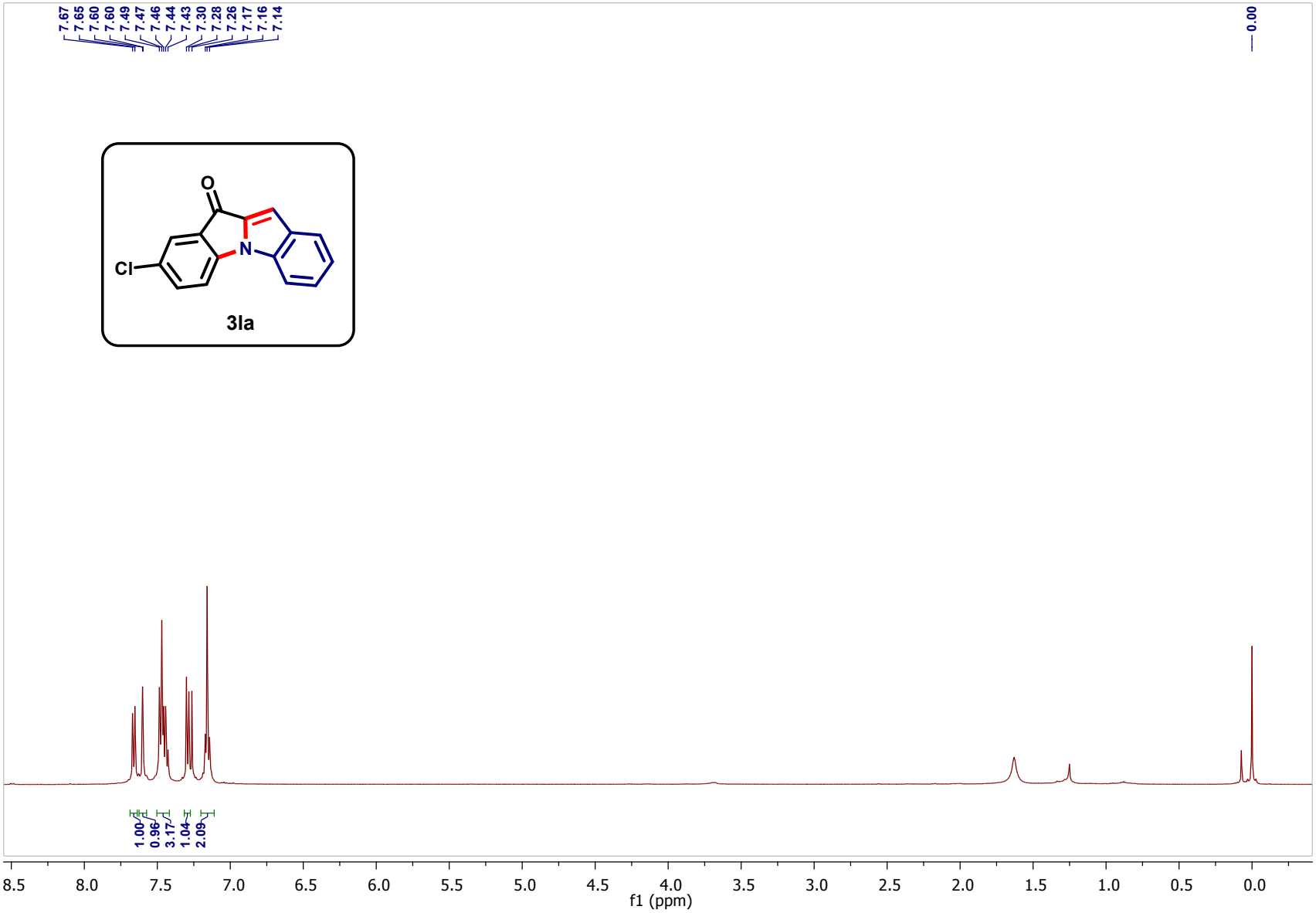
10
0
f1 (ppm)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7.30
7.28
7.26
7.17
7.16
7.14
0.00
O
Cl
N
3la
1.00
0.96
3.17
1.04
2.09
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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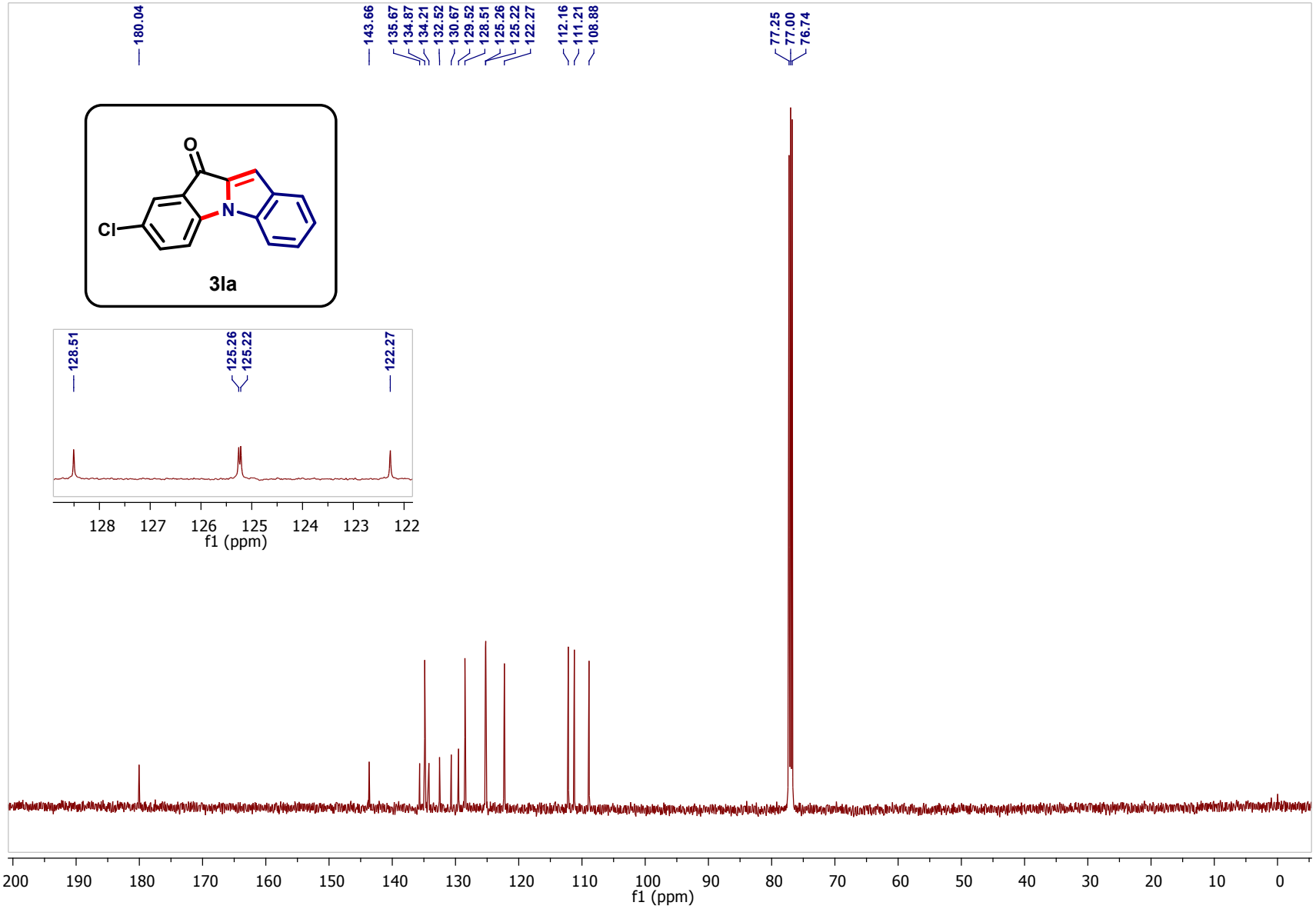
0.0
f1 (ppm)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132.52
130.67
129.52
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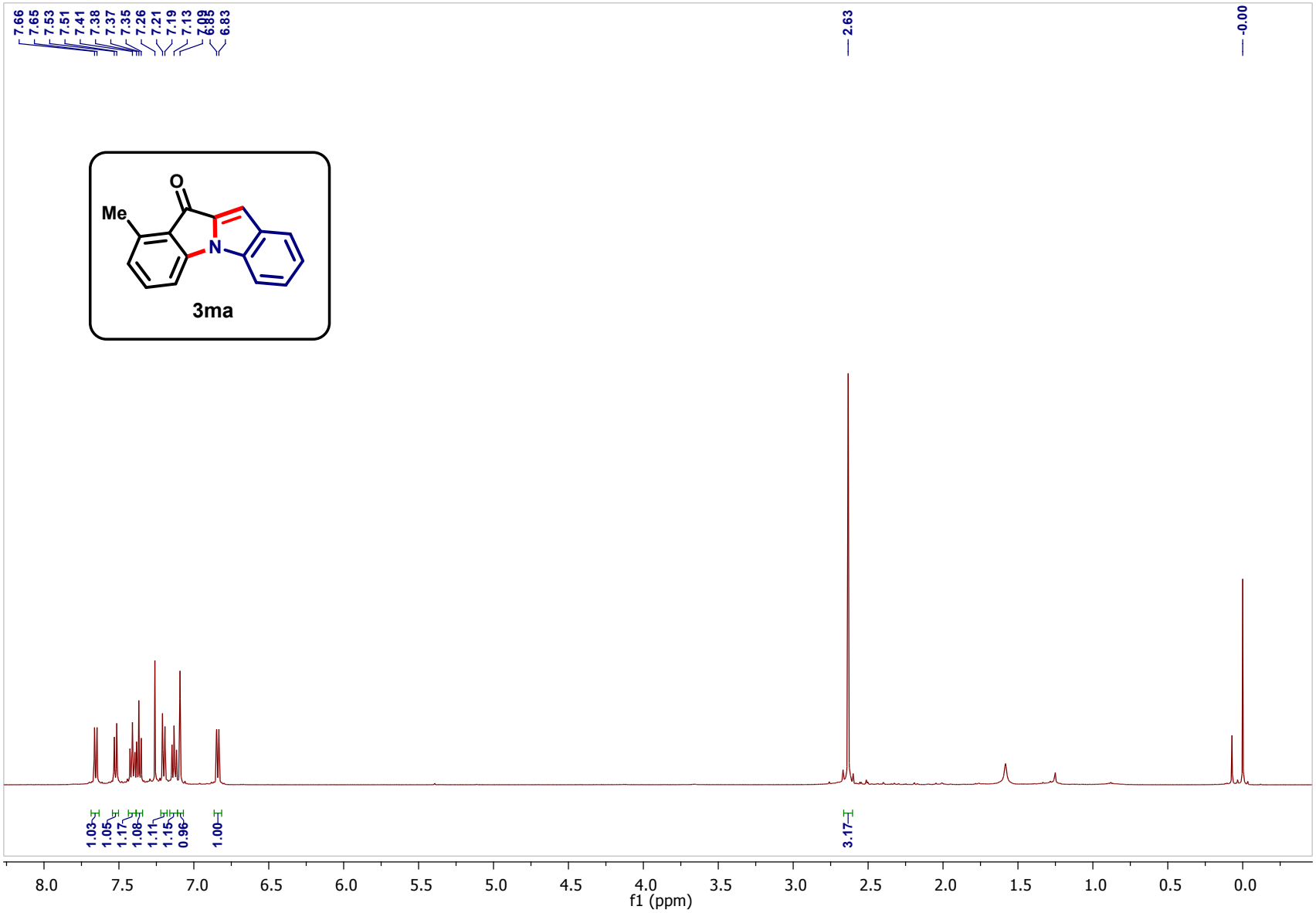
125.26
125.22
122.27
112.16
111.21
108.88
77.25
77.00
76.74
O
N
Cl
3la
128.51
125.26
125.22
122.27
128
127
126
125
124
123
122
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.51
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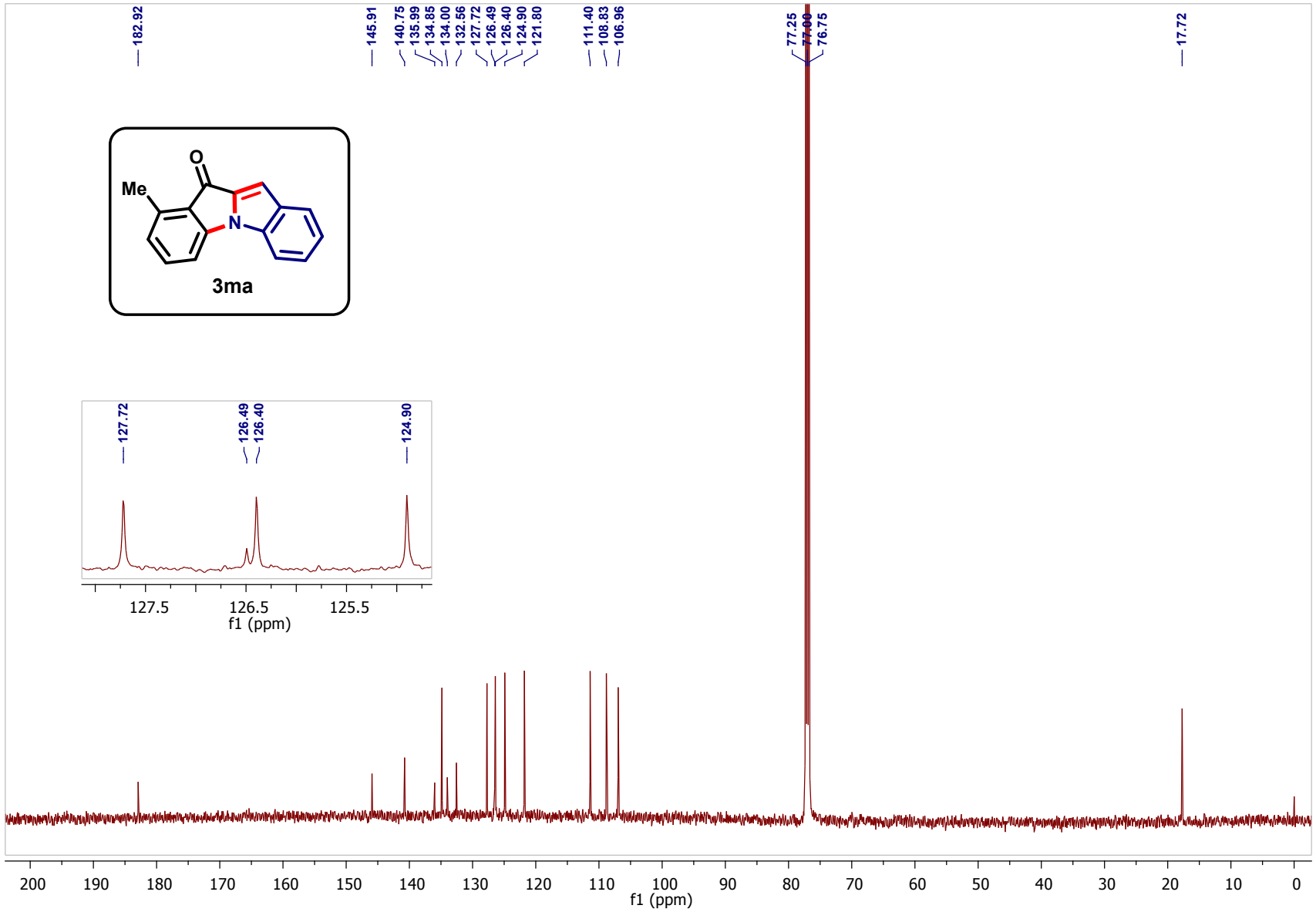
7.38
7.37
7.35
7.26
7.21
7.19
7.13
7.09
6.85
6.83
2.63
-0.00
O
Me
N
3ma
1.03
1.05
1.17
1.08
1.11
1.15
0.98
1.00
3.17
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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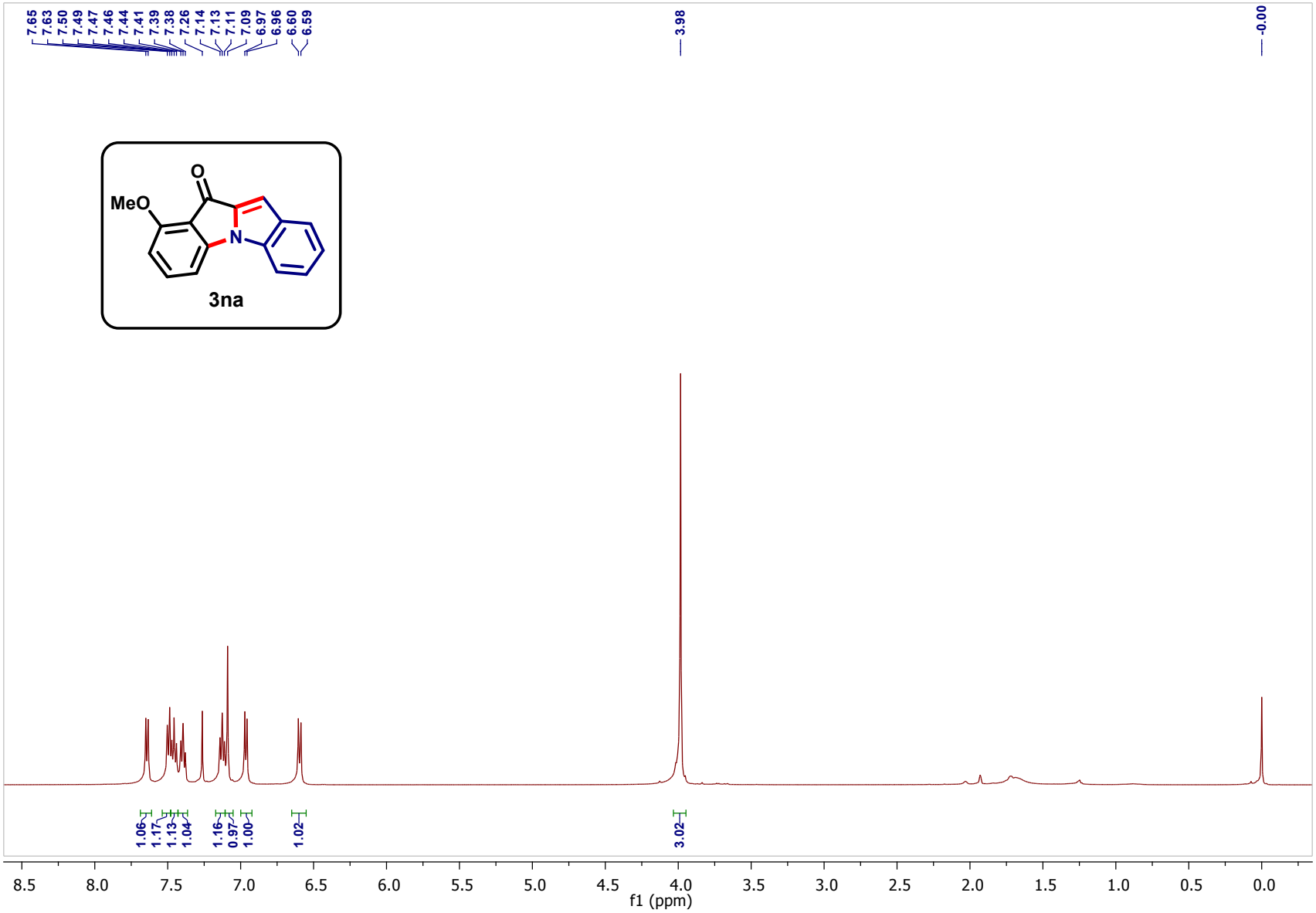
134.85
134.00
132.56
127.72
126.49
126.40
124.90
121.80
111.40
108.83
106.96
77.25
77.00
76.75
17.72
O
Me
N
3ma
127.72
126.49
126.40
124.90
127.5
126.5
125.5
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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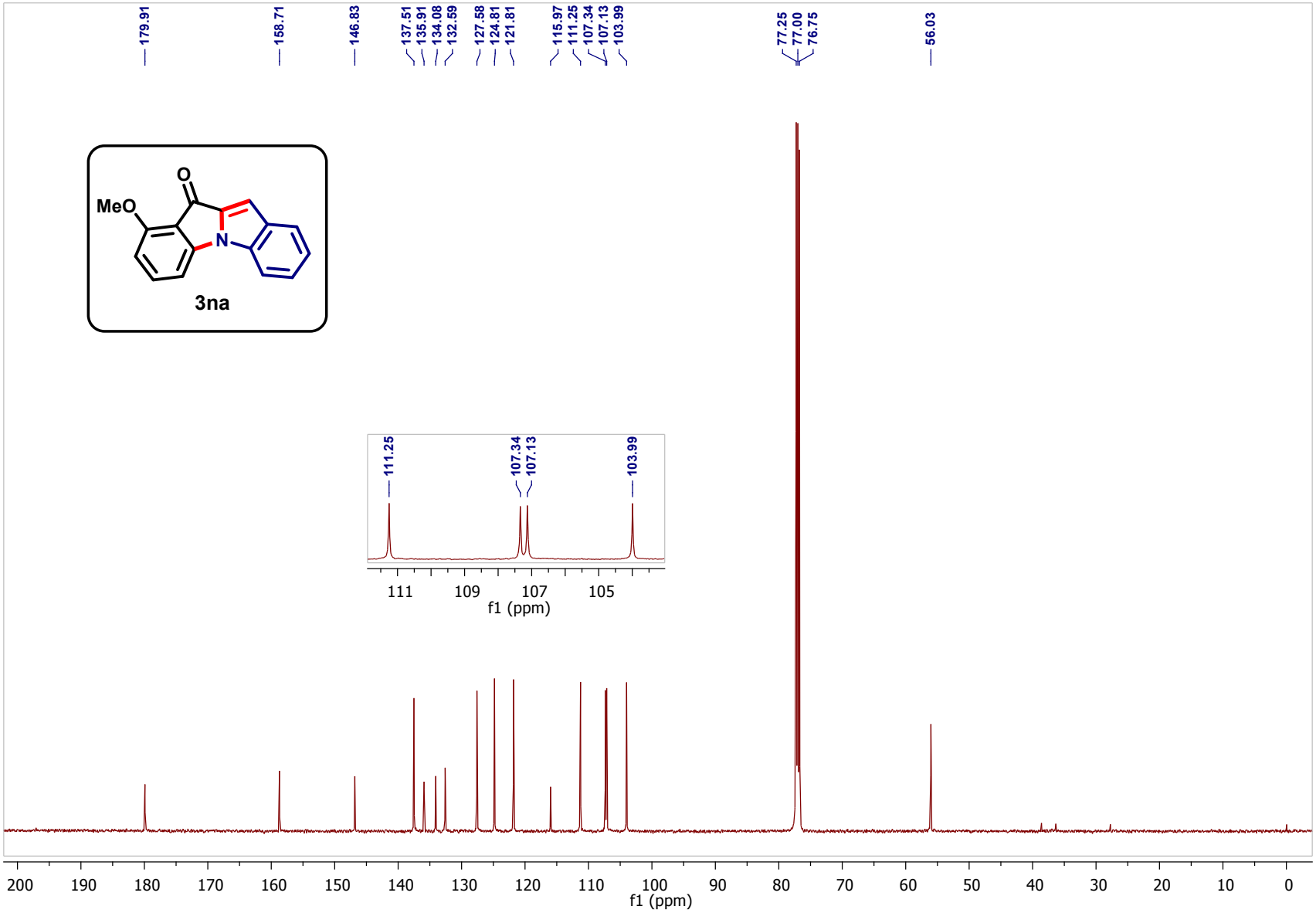
7.63
7.50
7.49
7.47
7.46
7.44
7.41
7.39
7.38
7.26
7.14
7.13
7.11
7.09
6.97
6.96
6.60
6.59
3.98
-0.00
O
MeO
N
3na
1.06
1.17
1.13
1.04
1.16
0.97
1.00
1.02
3.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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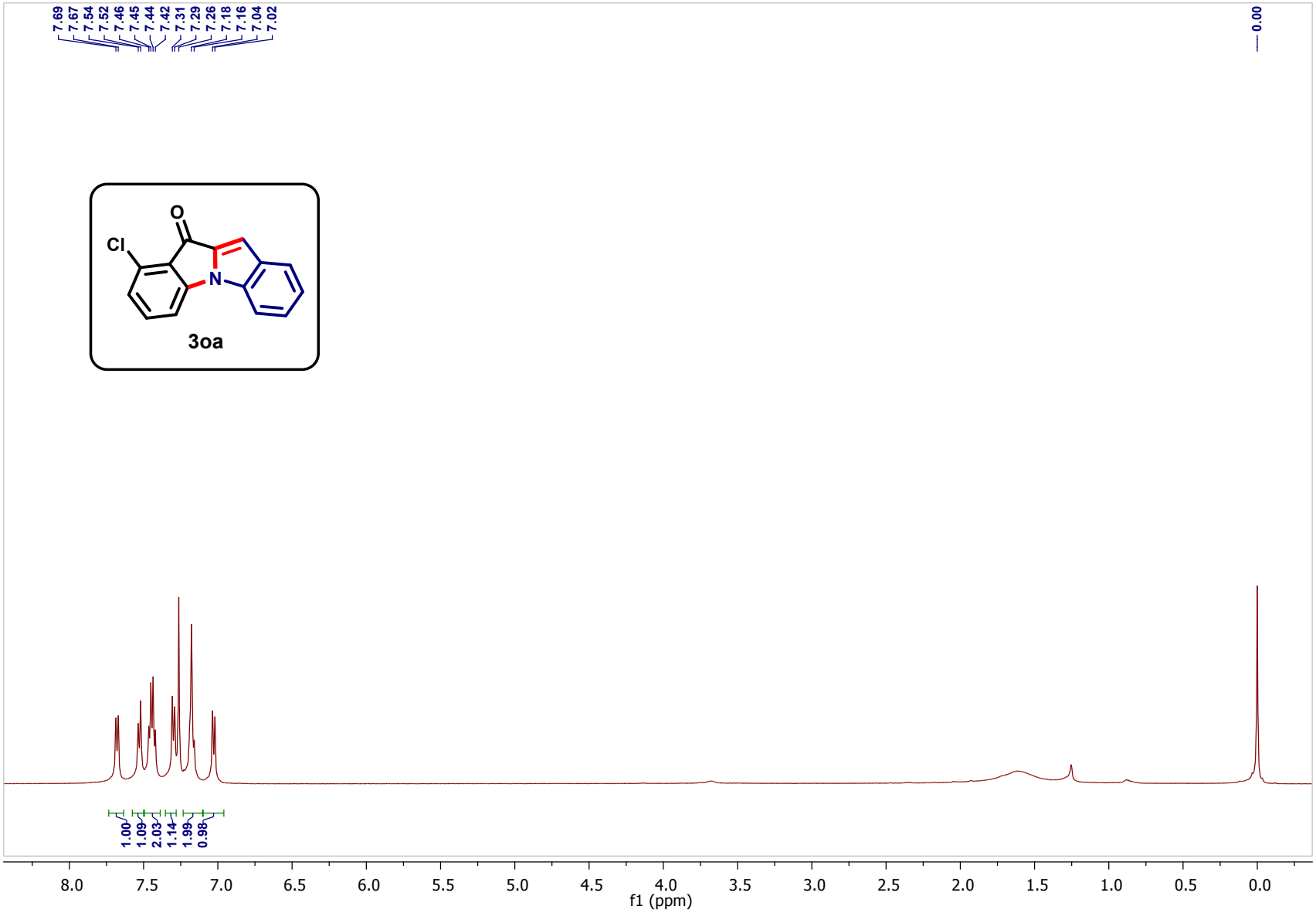
158.71
146.83
137.51
135.91
134.08
132.59
127.58
124.81
121.81
115.97
111.25
107.34
107.13
103.99
77.25
77.00
76.75
56.03
MeO
O
N
3na
111.25
107.34
107.13
103.99
111
109
107
105
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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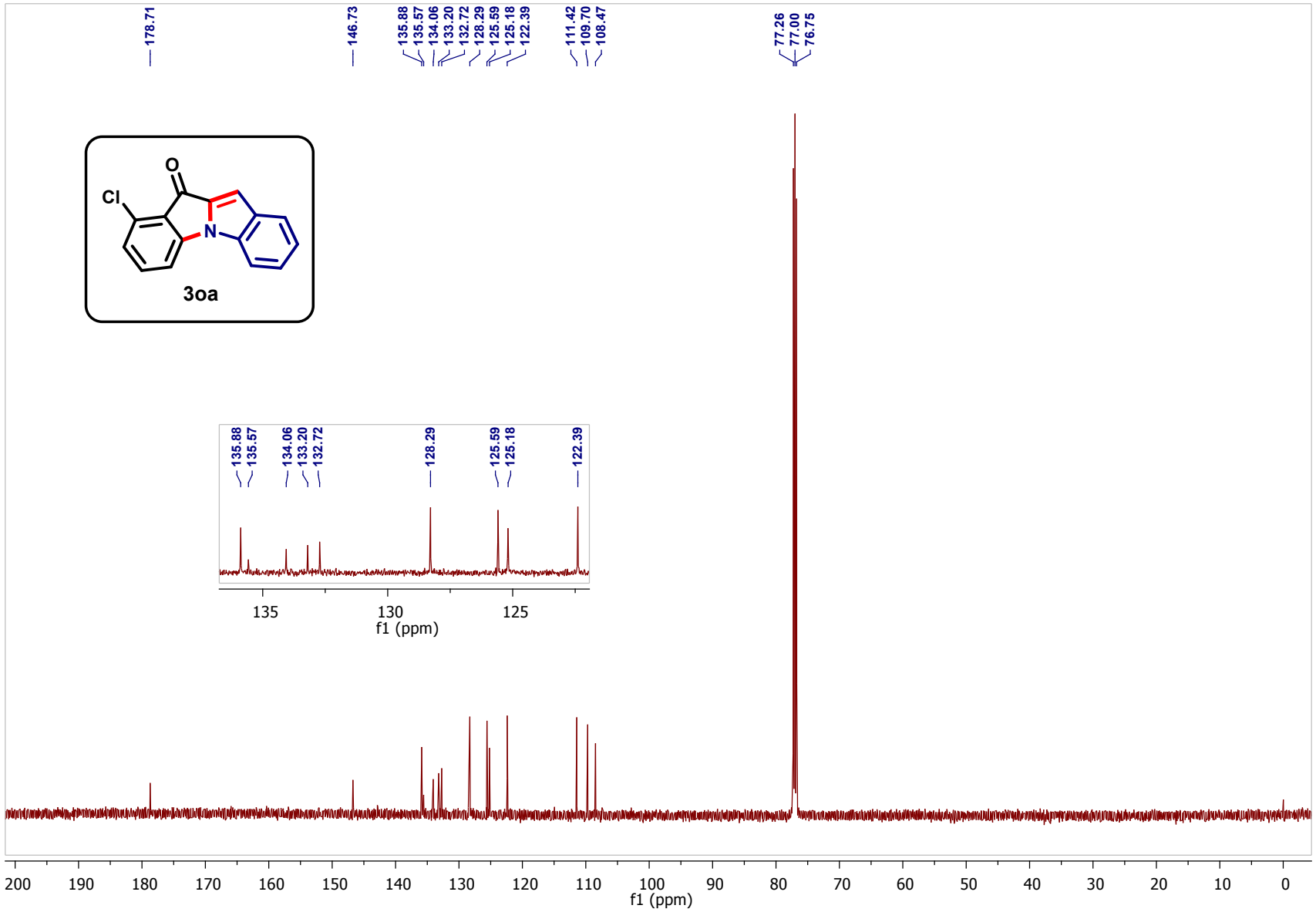
7.45
7.44
7.42
7.31
7.29
7.26
7.18
7.16
7.04
7.02
0.00
O
Cl
N
3oa
1.00
1.09
2.03
1.14
1.99
0.98
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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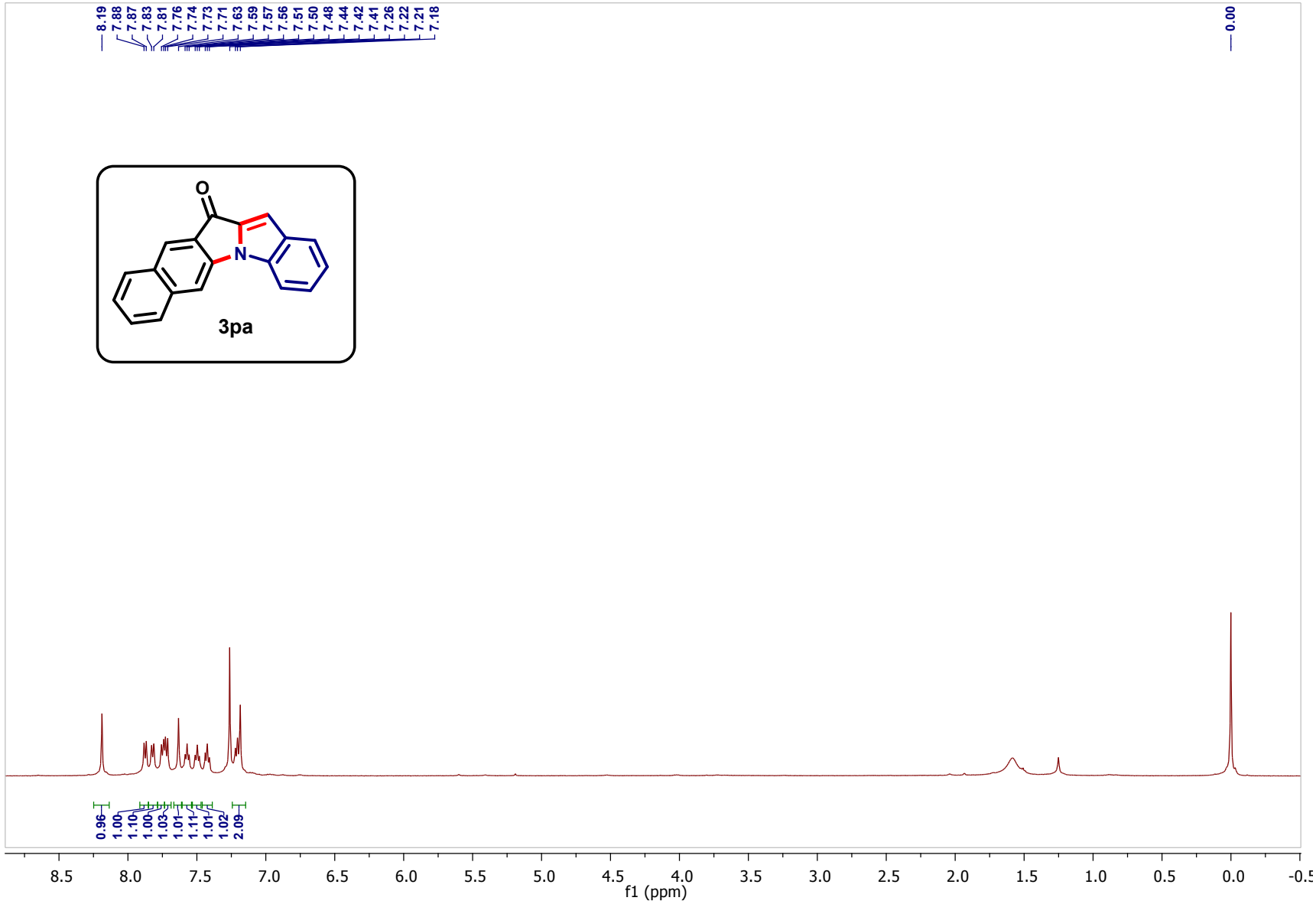
133.20
132.72
128.29
125.59
125.18
122.39
111.42
109.70
108.47
77.26
77.00
76.75
O
Cl
N
3oa
135
130
125
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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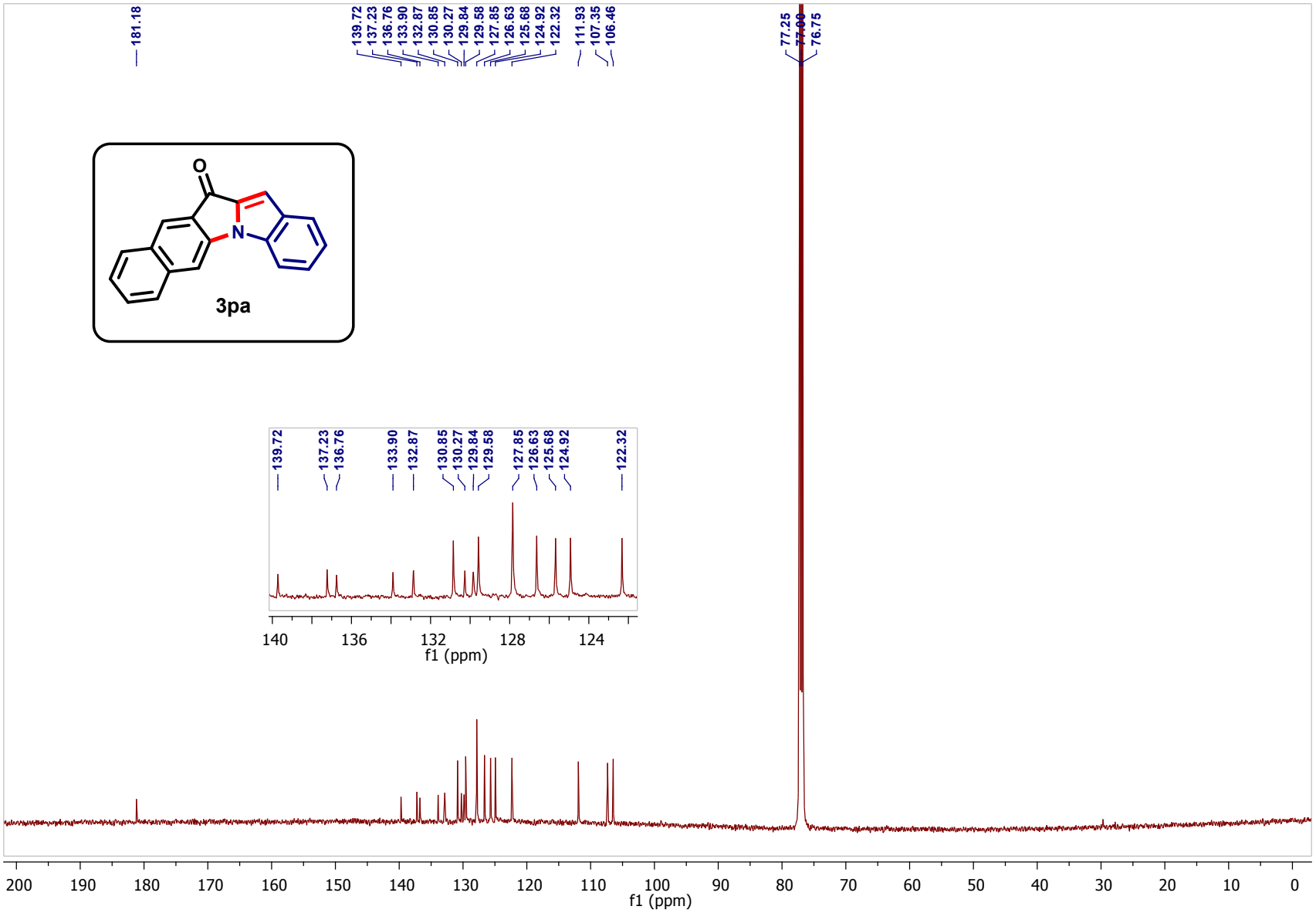
7.87
7.83
7.81
7.76
7.74
7.73
7.71
7.63
7.59
7.57
7.56
7.51
7.50
7.48
7.44
7.42
7.41
7.26
7.22
7.21
7.18
0.00
O
N
3pa
0.96
1.00
1.10
1.00
1.03
1.01
1.11
1.01
1.02
2.09
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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132.87
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130.27
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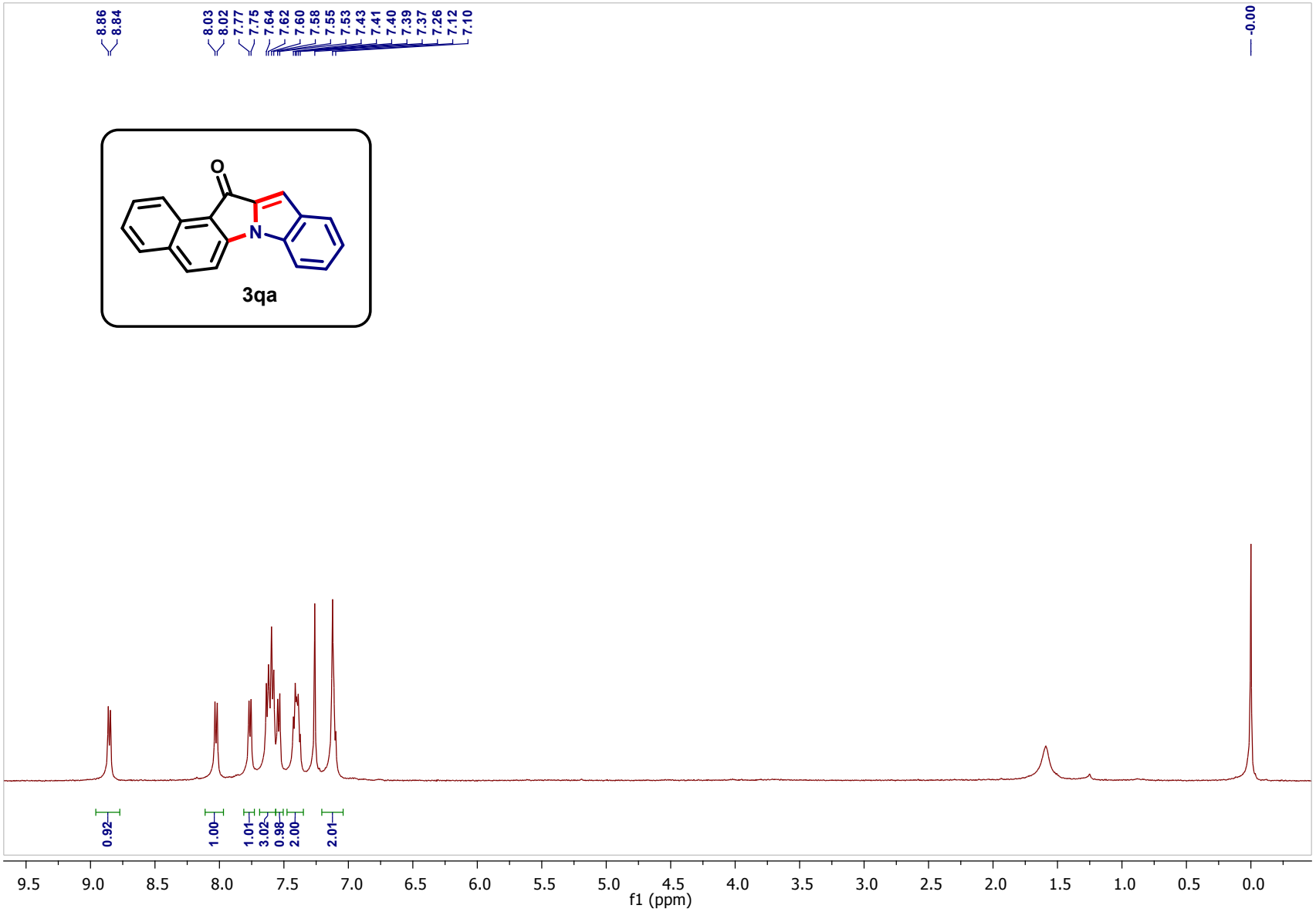
129.58
127.85
126.63
125.68
124.92
122.32
111.93
107.35
106.46
77.25
77.00
76.75
O
N
3pa
f1 (ppm)
f1 (ppm)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8.84
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8.02
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7.62
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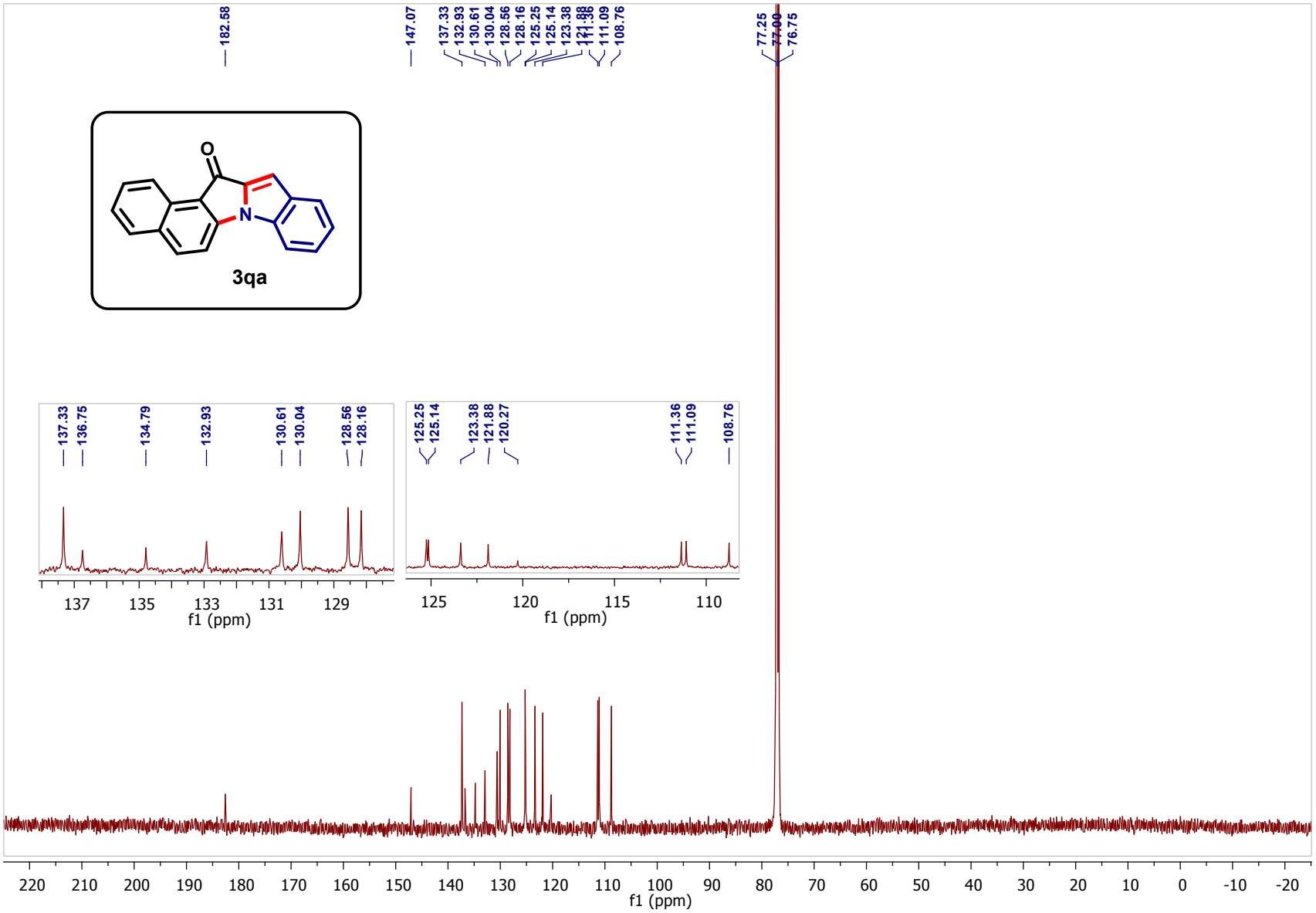
7.58
7.55
7.53
7.43
7.41
7.40
7.39
7.37
7.26
7.12
7.10
-0.00
O
N
3qa
0.92
1.00
1.01
3.02
0.98
2.00
2.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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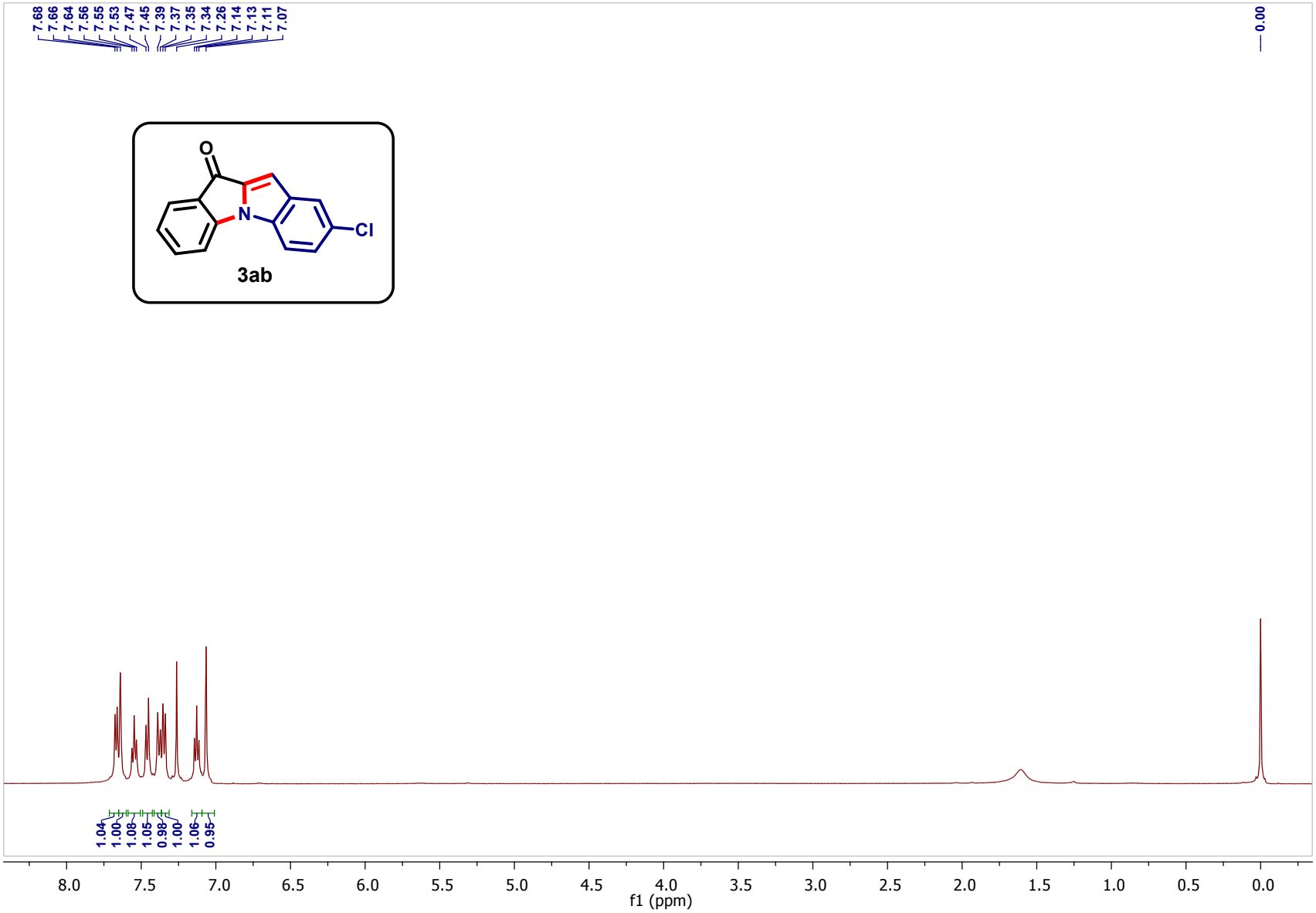
125.14
123.38
121.88
111.36
111.09
108.76
77.25
77.00
76.75
O
N
3qa
137.33
136.75
134.79
132.93
130.61
130.04
128.56
128.16
125.25
125.14
123.38
121.88
120.27
111.36
111.09
108.76
137
135
133
131
129
f1 (ppm)
125
120
115
110
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)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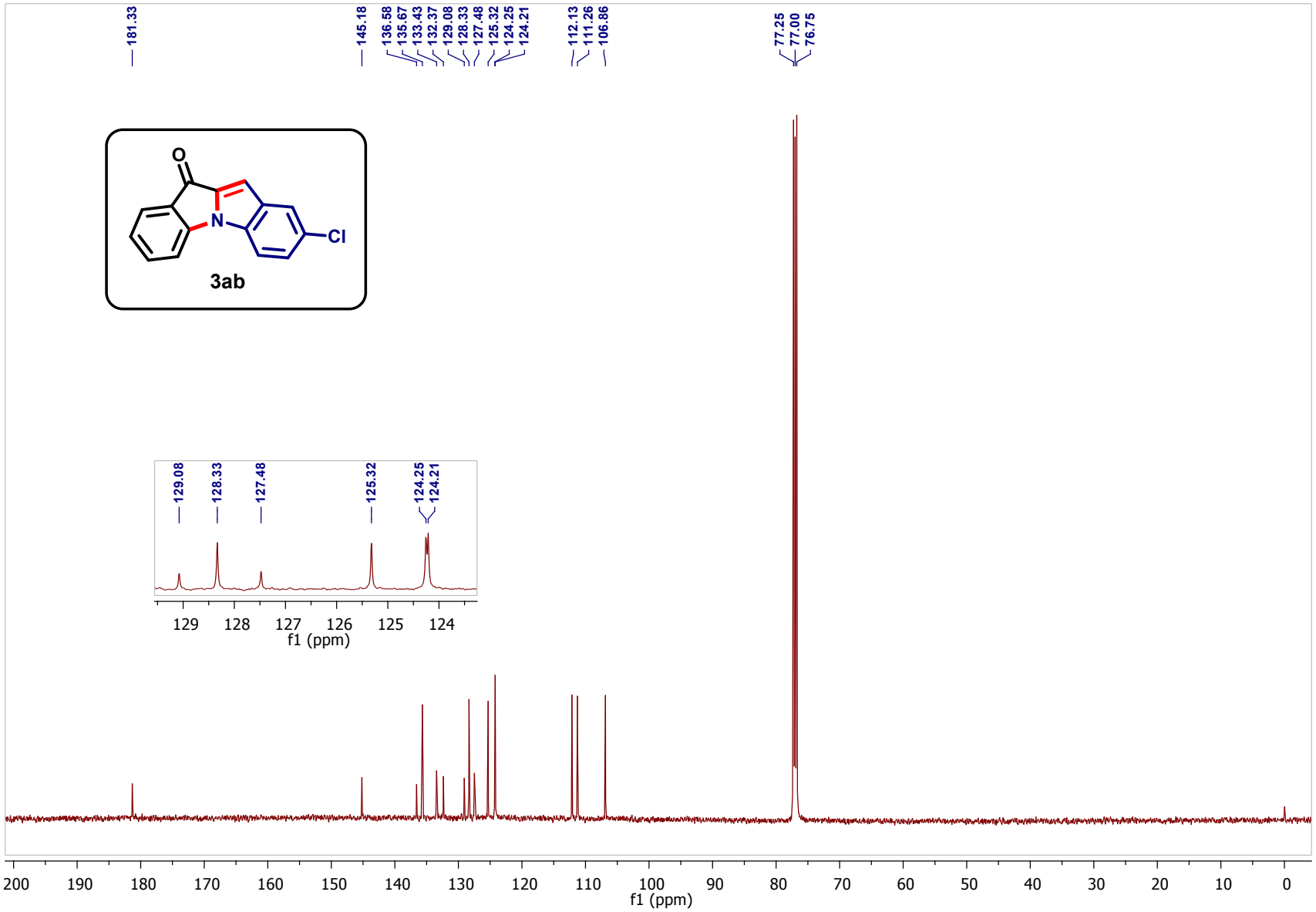
7.34
7.26
7.14
7.13
7.11
7.07
0.00
O
N
Cl
3ab
1.04
1.00
1.08
1.05
0.98
1.00
1.06
0.95
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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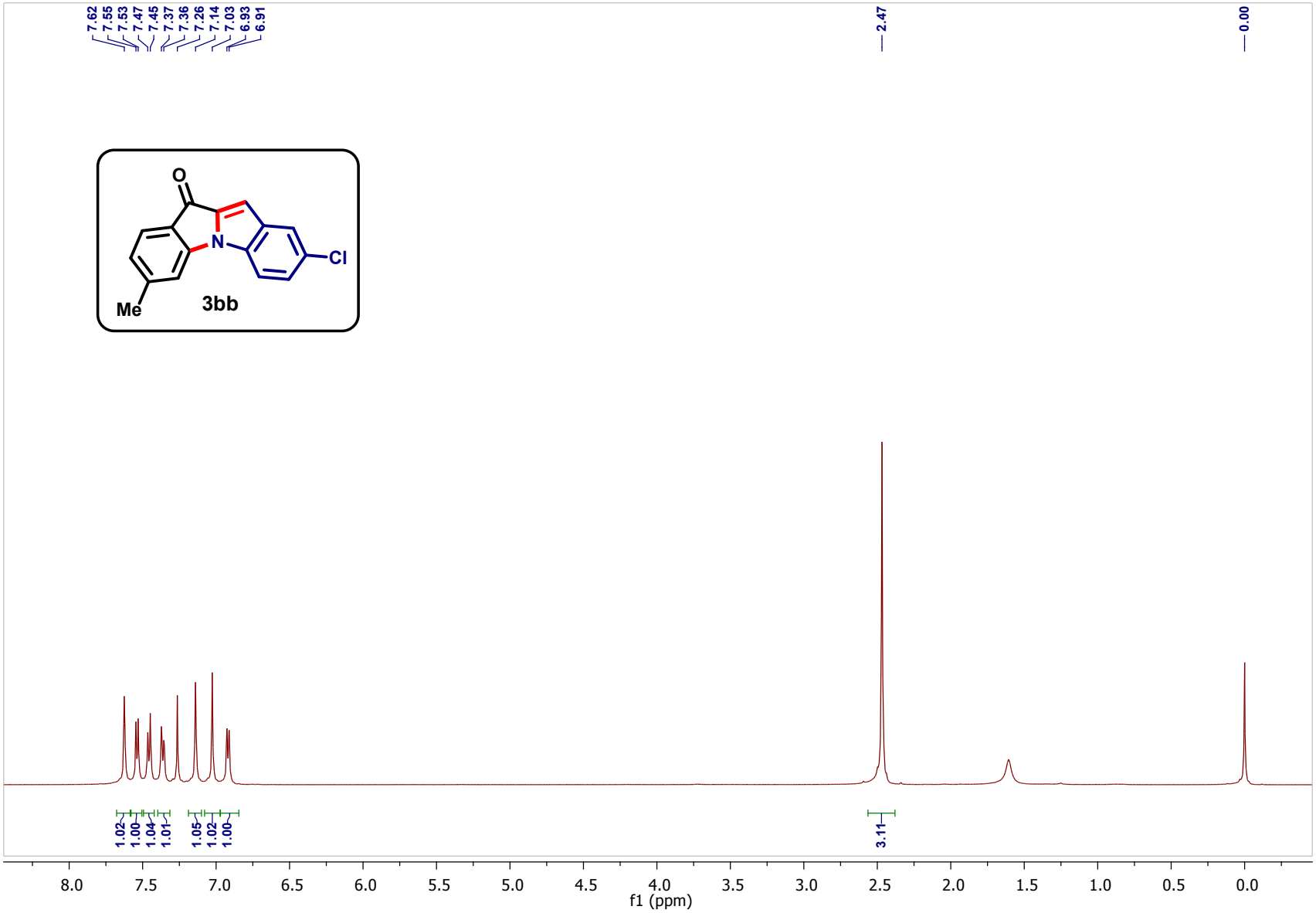
128.33
127.48
125.32
124.25
124.21
112.13
111.26
106.86
77.25
77.00
76.75
O
N
Cl
3ab
129.08
128.33
127.48
125.32
124.25
124.21
129
128
127
126
125
124
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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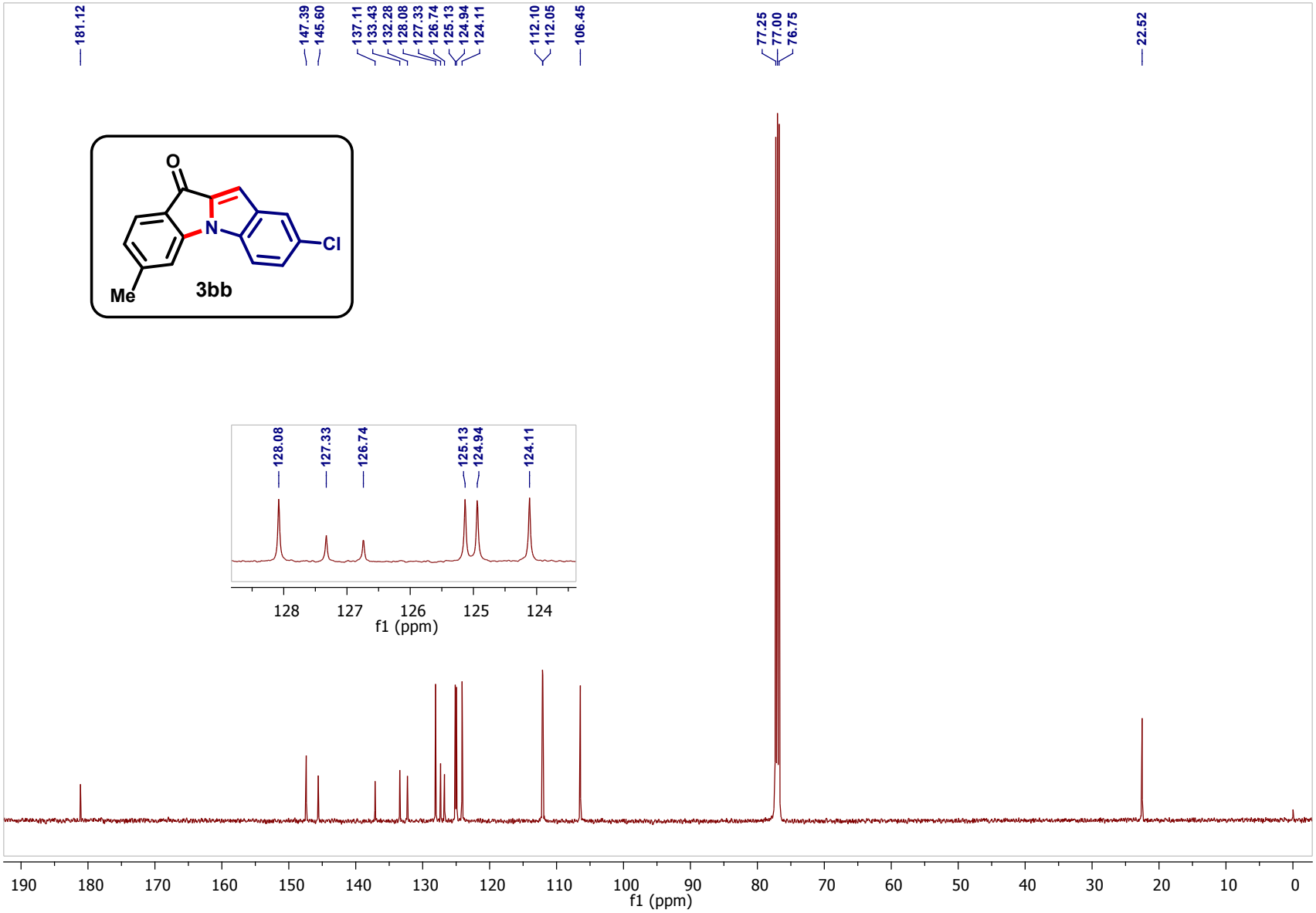
7.47
7.45
7.37
7.36
7.26
7.14
7.03
6.93
6.91
2.47
0.00
O
N
Cl
Me
3bb
1.02
1.00
1.04
1.01
1.05
1.02
1.00
3.11
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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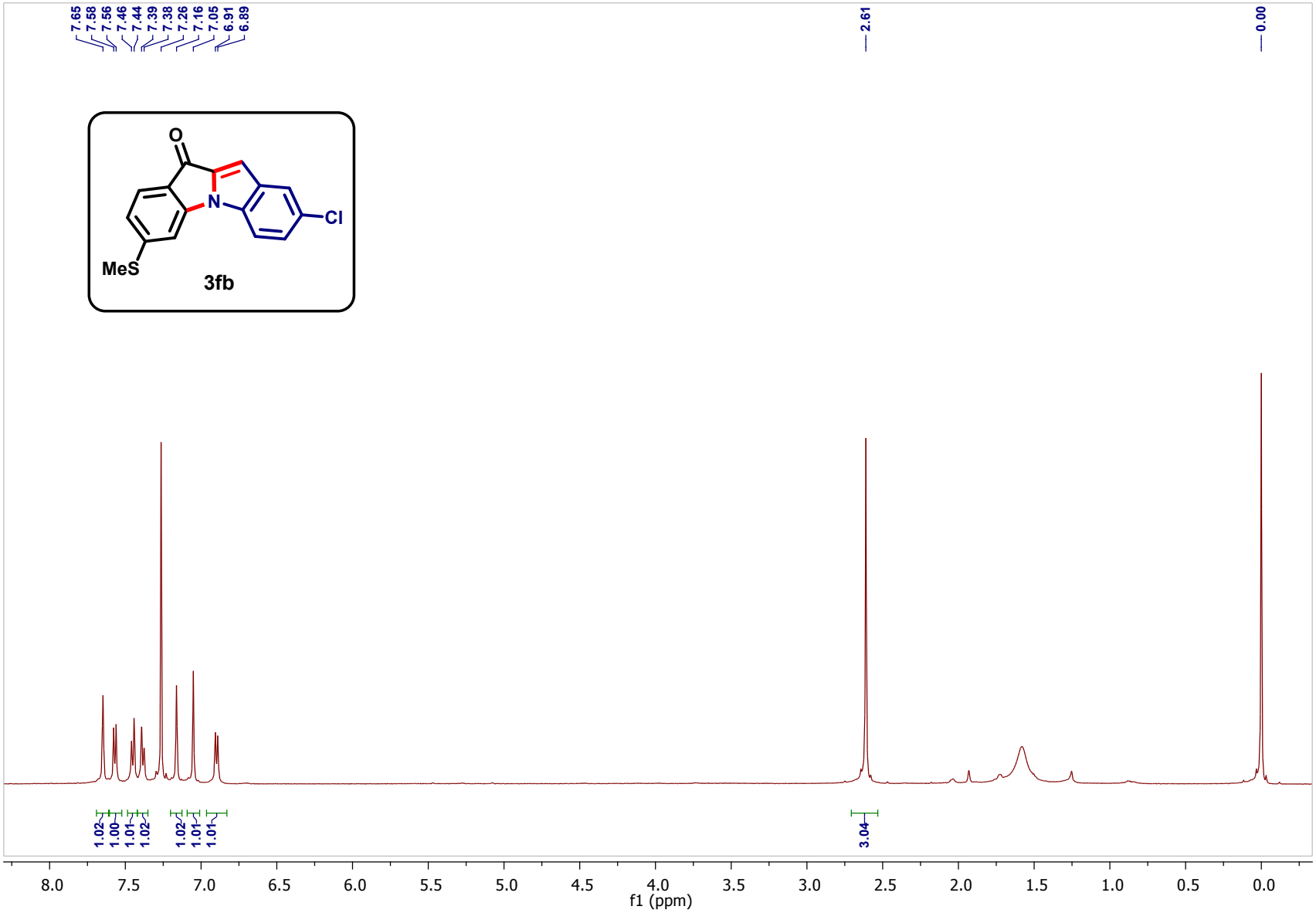
126.74
125.13
124.94
124.11
112.10
112.05
106.45
77.25
77.00
76.75
22.52
O
N
Cl
Me
3bb
128.08
127.33
126.74
125.13
124.94
124.11
128
127
126
125
124
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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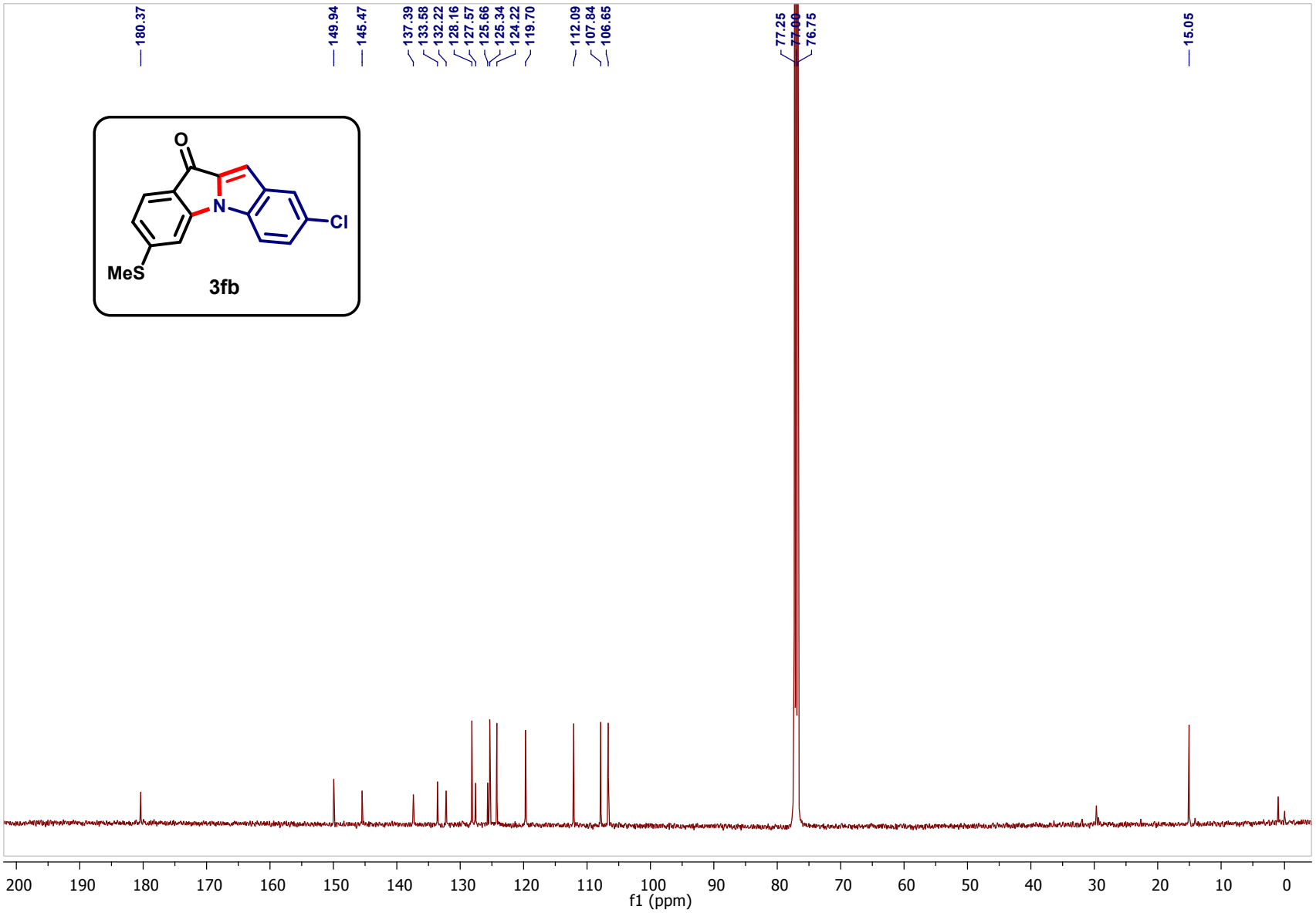
7.39
7.38
7.26
7.16
7.05
6.91
6.89
2.61
0.00
O
N
Cl
MeS
3fb
1.02
1.00
1.01
1.02
1.02
1.01
1.01
3.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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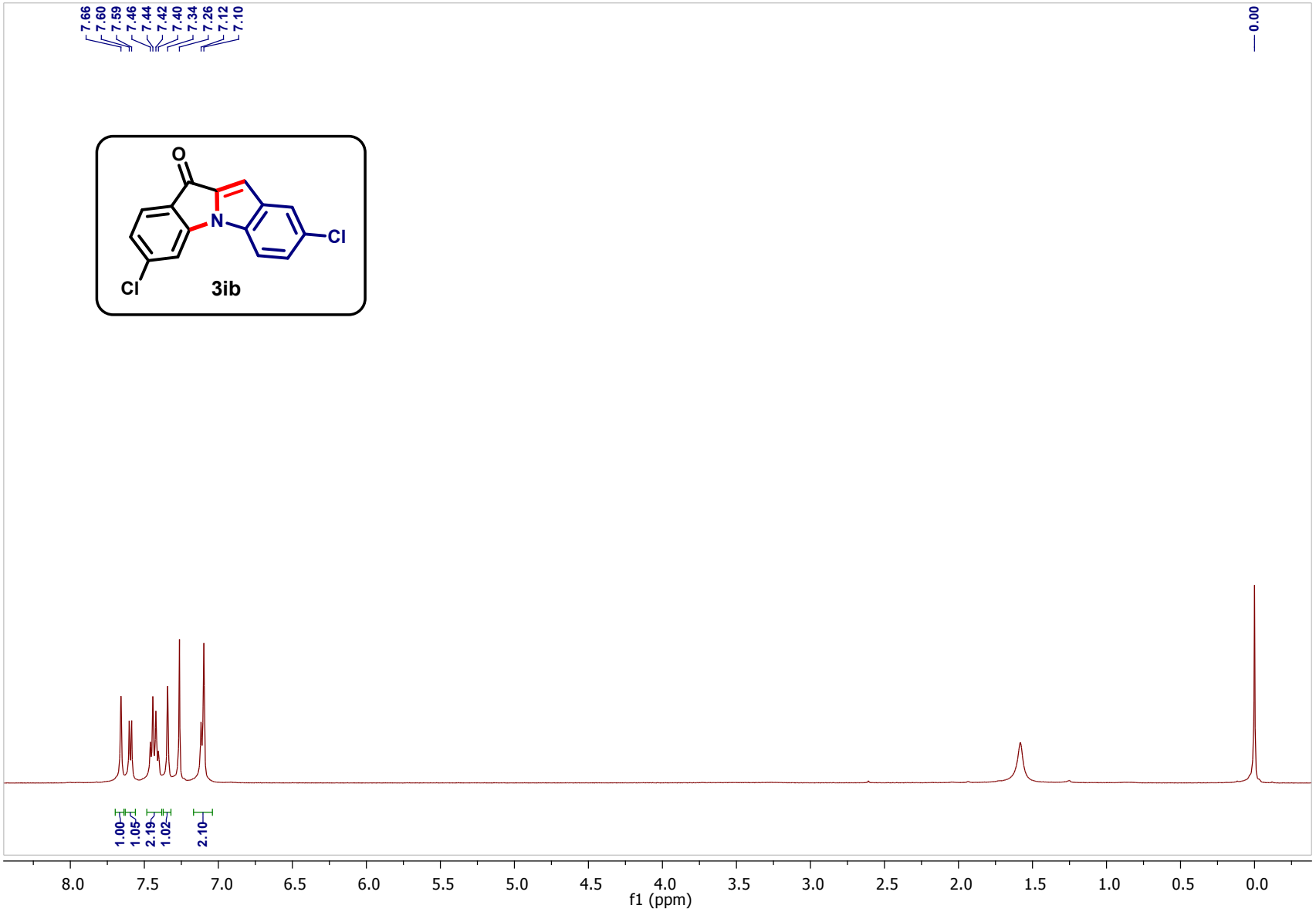
145.47
137.39
133.58
132.22
128.16
127.57
125.66
125.34
124.22
119.70
112.09
107.84
106.65
77.25
77.00
76.75
15.05
O
N
Cl
MeS
3fb
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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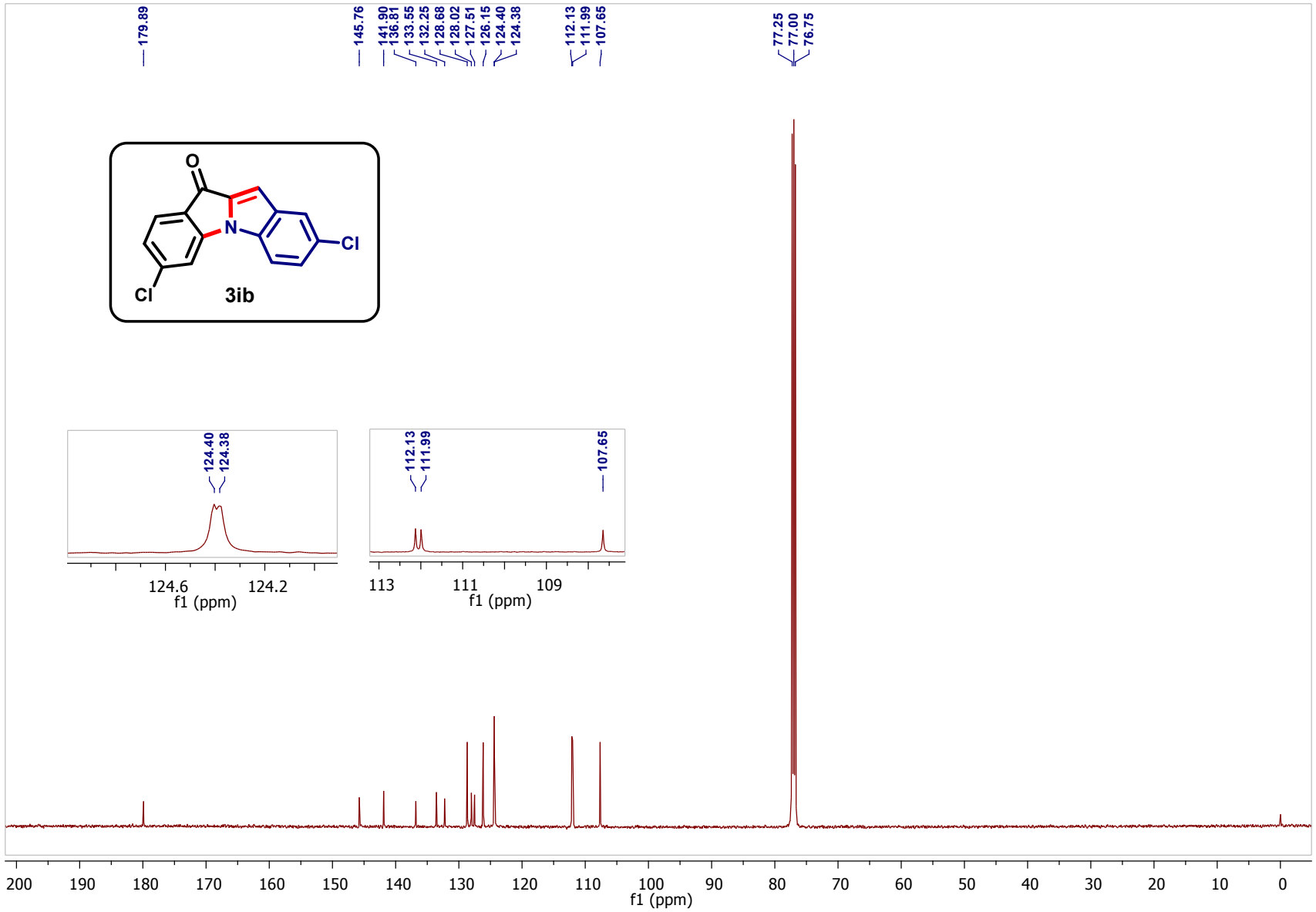
7.34
7.26
7.12
7.10
0.00
O
N
Cl
Cl
3ib
1.00
1.05
2.19
1.02
2.10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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141.90
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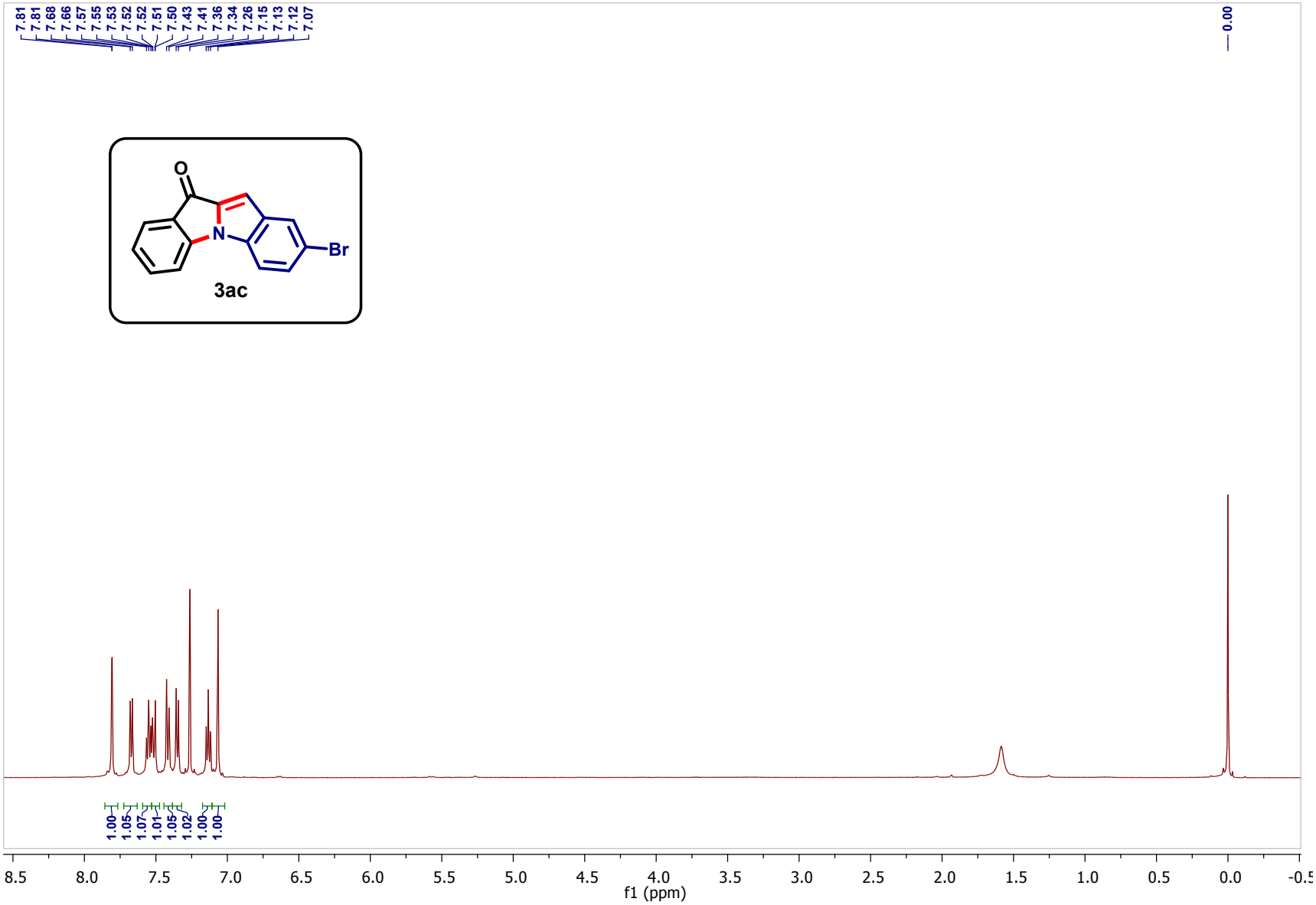
133.55
132.25
128.68
128.02
127.51
126.15
124.40
124.38
112.13
111.99
107.65
77.25
77.00
76.75
O
N
Cl
Cl
3ib
124.40
124.38
124.6
124.2
f1 (ppm)
112.13
111.99
107.65
113
111
109
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.52
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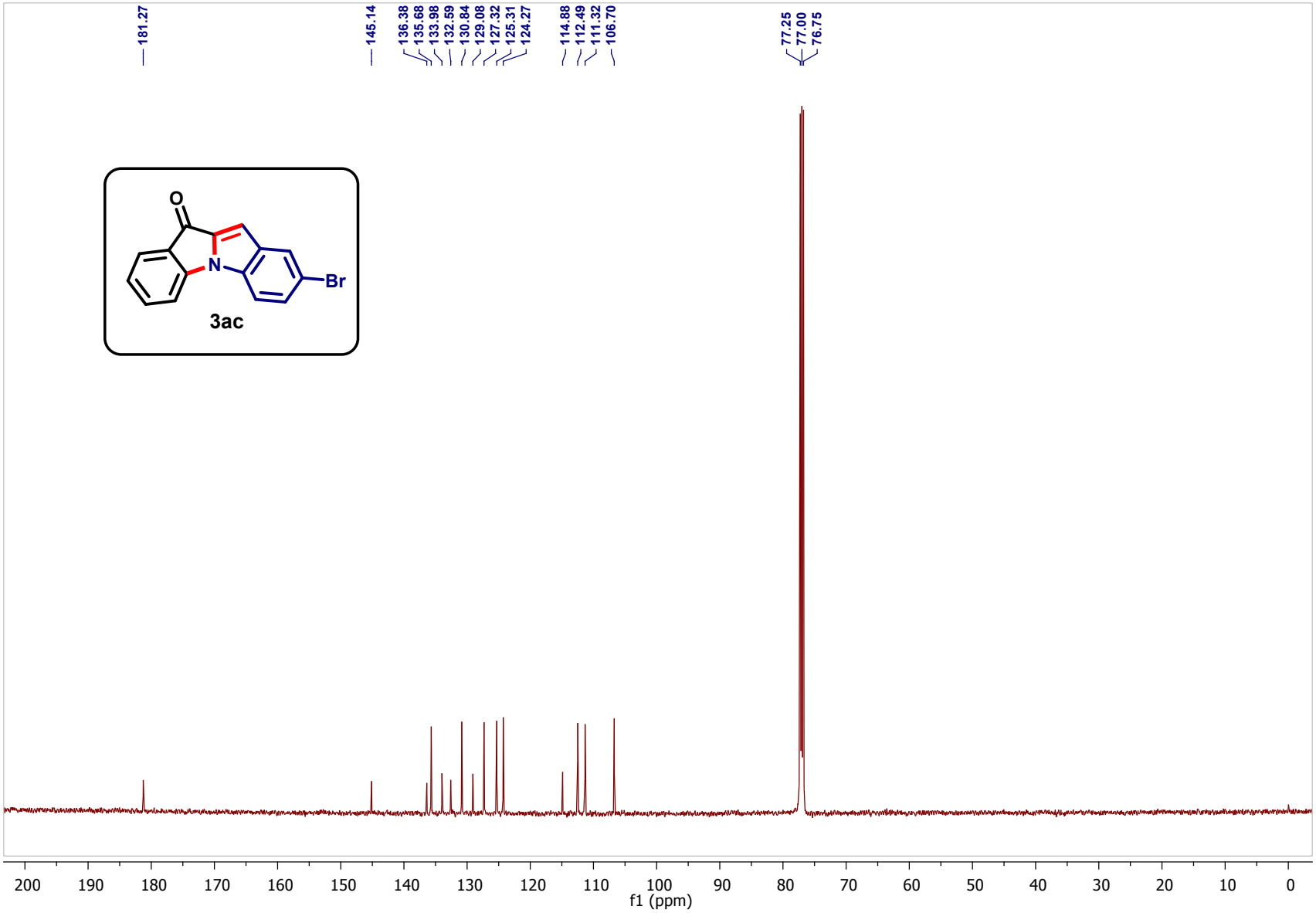
7.51
7.50
7.43
7.41
7.36
7.34
7.26
7.15
7.13
7.12
7.07
0.00
O
N
Br
3ac
1.00
1.05
1.07
1.01
1.05
1.02
1.00
1.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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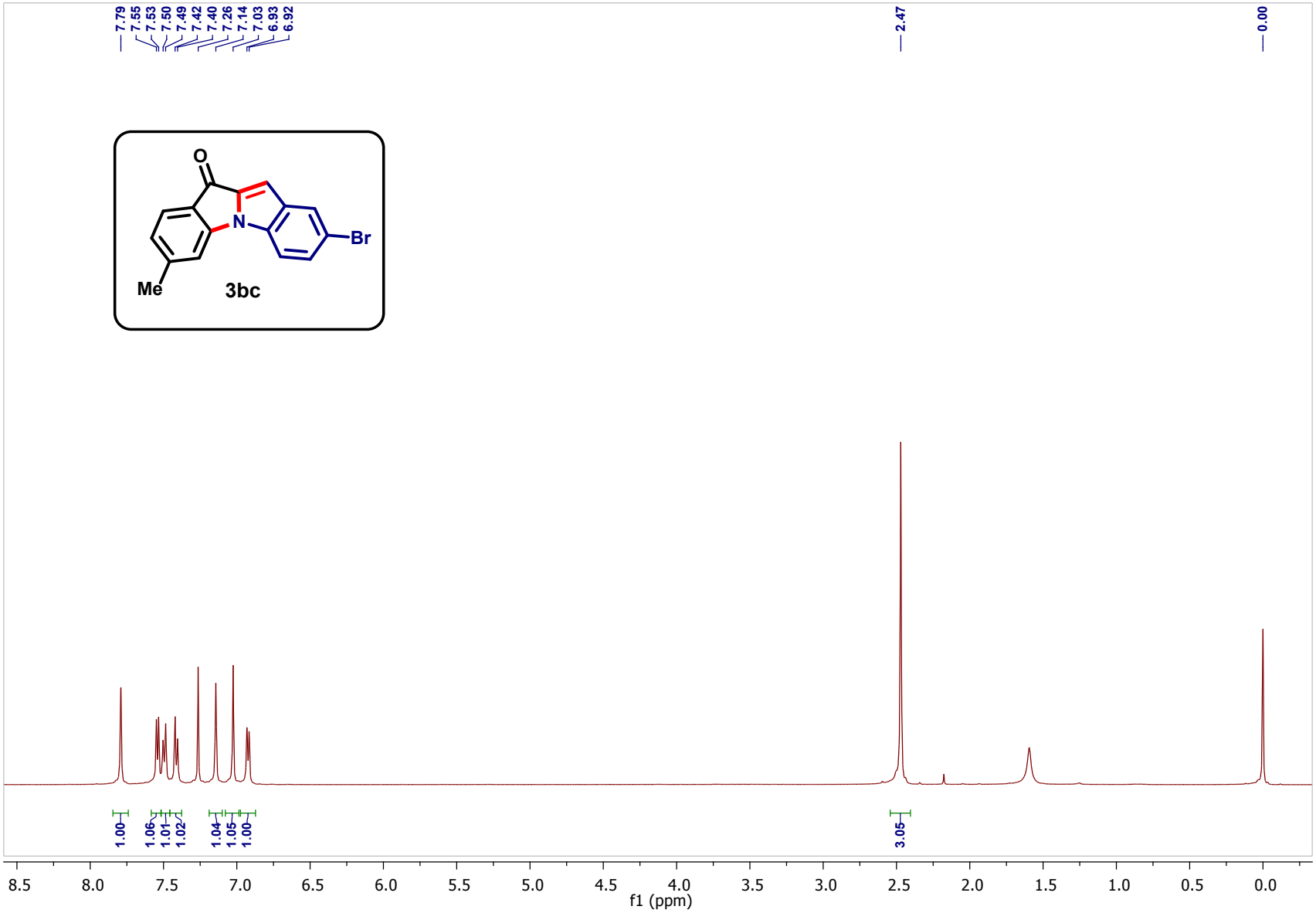
136.38
135.68
133.98
132.59
130.84
129.08
127.32
125.31
124.27
114.88
112.49
111.32
106.70
77.25
77.00
76.75
O
N
Br
3ac
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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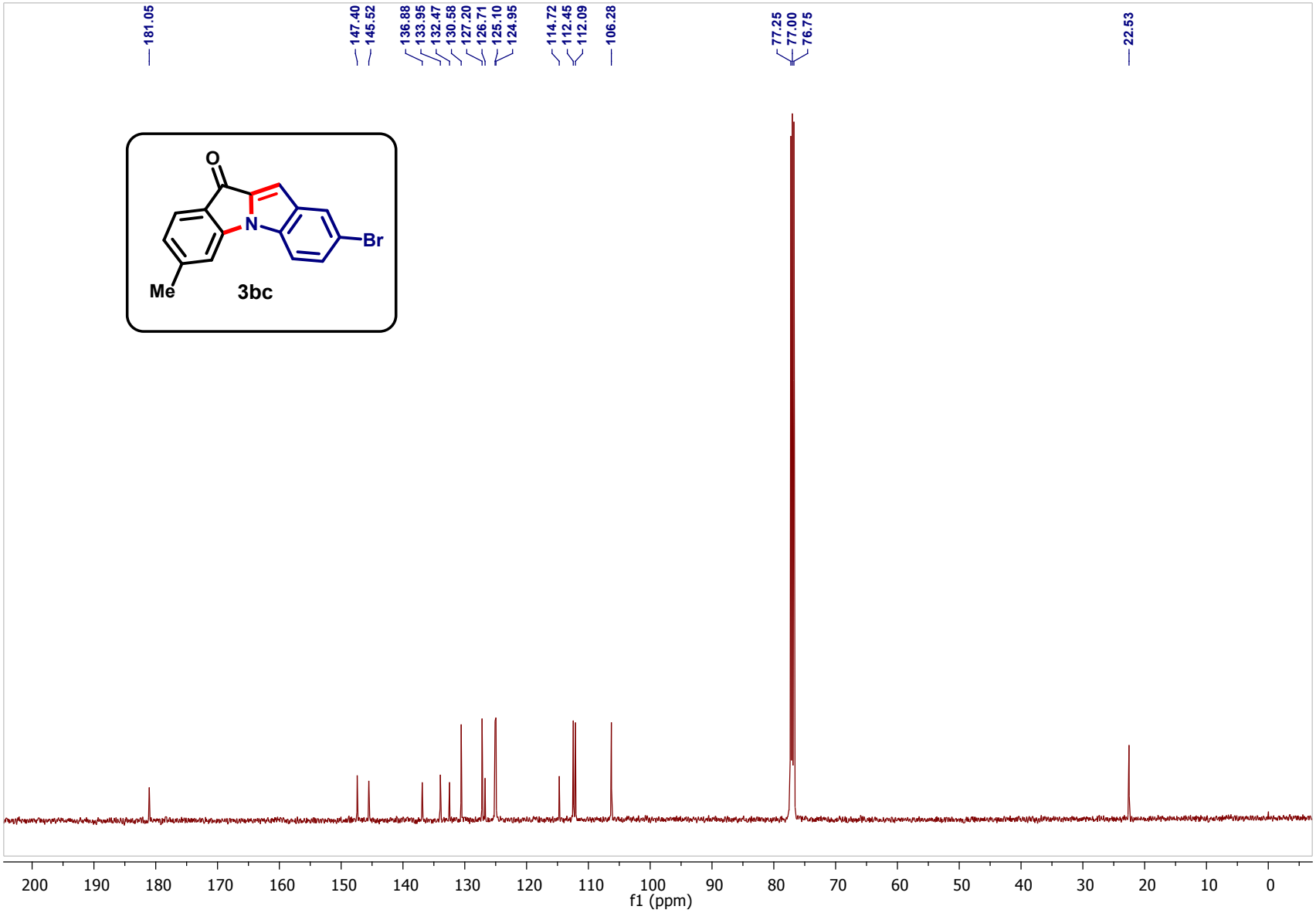
7.55
7.53
7.50
7.49
7.42
7.40
7.26
7.14
7.03
6.93
6.92
2.47
0.00
O
N
Br
Me
3bc
1.00
1.06
1.01
1.02
1.04
1.05
1.00
3.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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147.40
145.52
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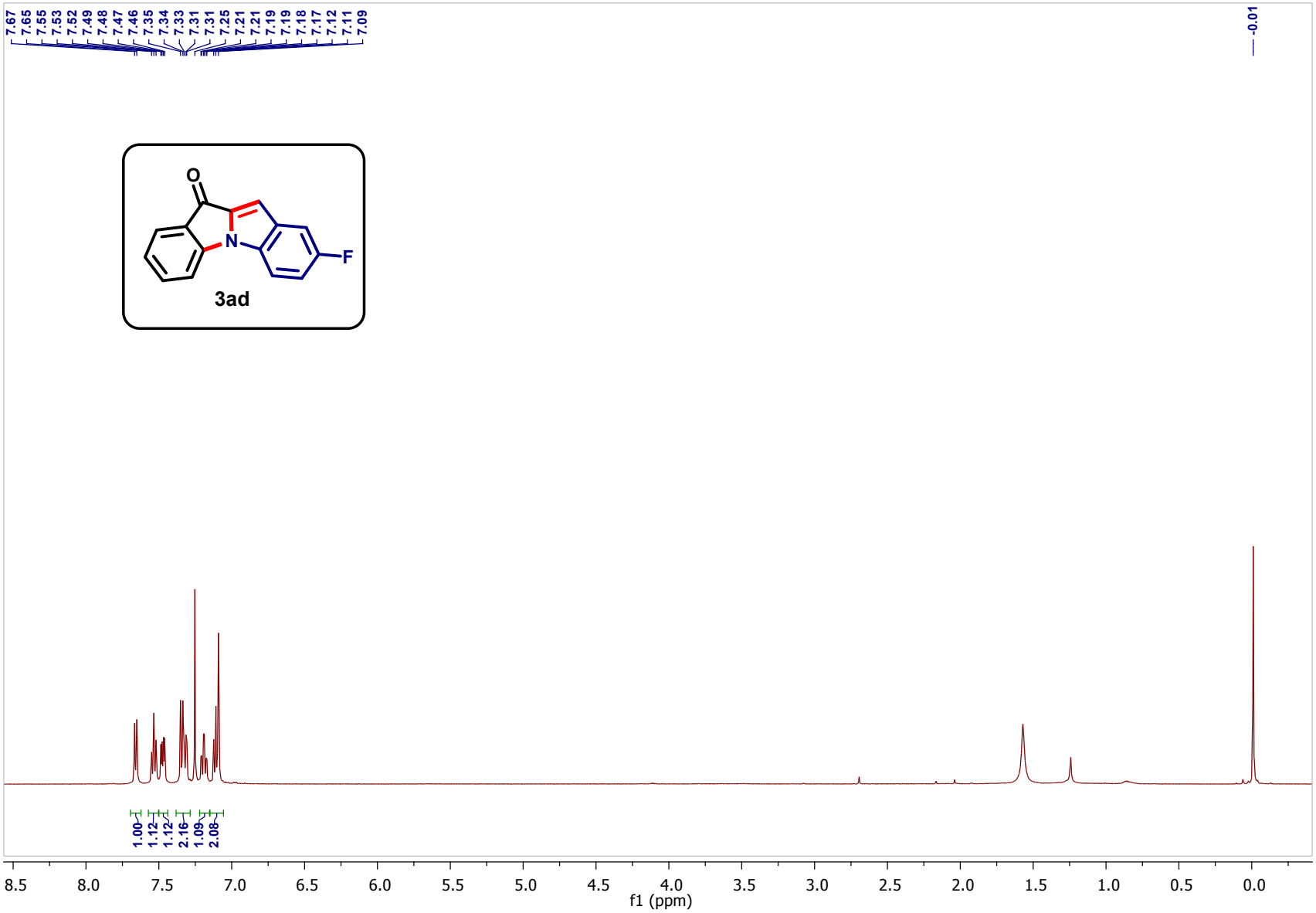
132.47
130.58
127.20
126.71
125.10
124.95
114.72
112.45
112.09
106.28
77.25
77.00
76.75
22.53
O
N
Br
Me
3bc
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.53
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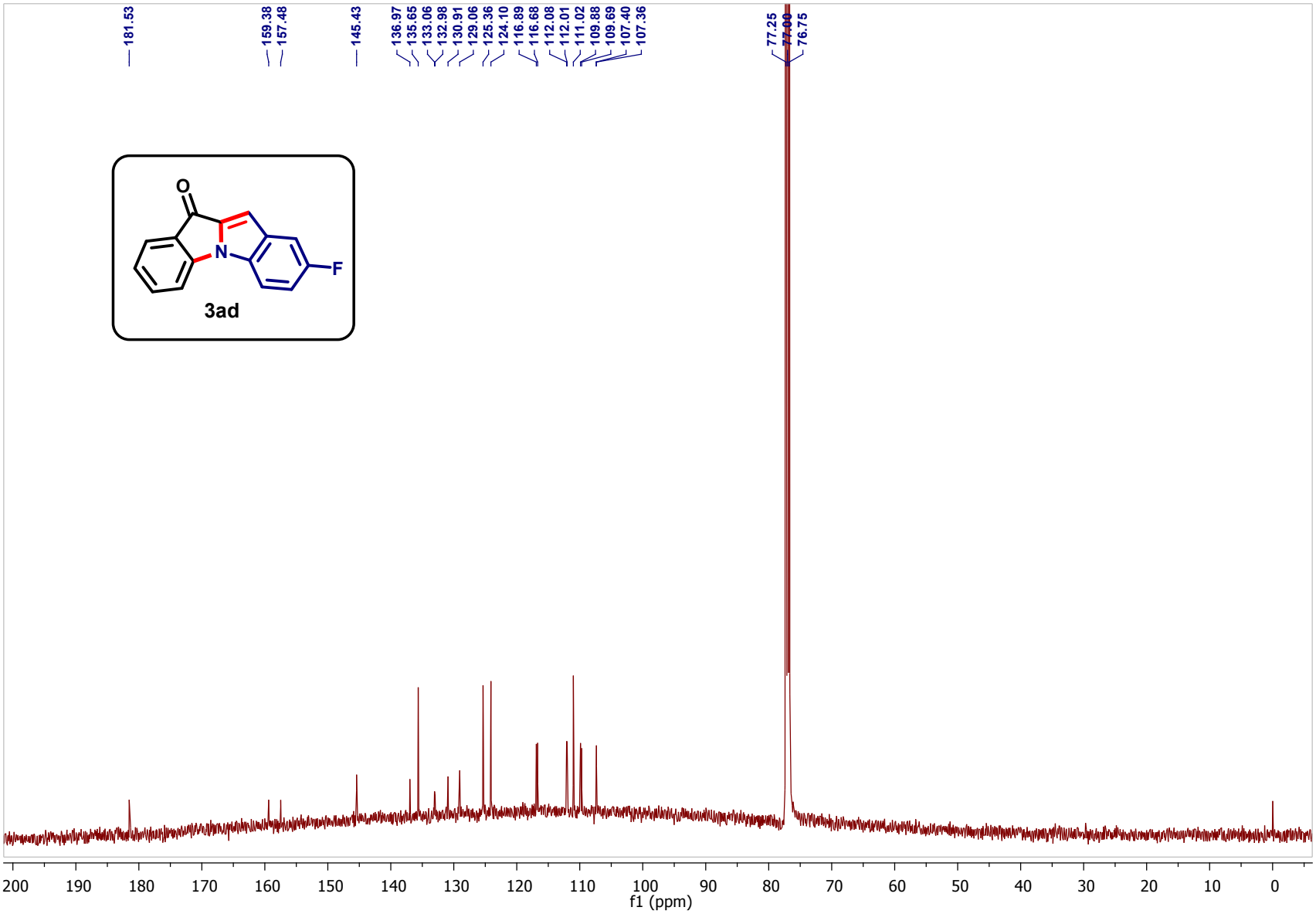
7.49
7.48
7.47
7.46
7.35
7.34
7.33
7.31
7.31
7.25
7.21
7.21
7.19
7.19
7.18
7.17
7.12
7.11
7.09
-0.01
O
N
F
3ad
1.00
1.12
1.12
2.16
1.09
2.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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159.38
157.48
145.43
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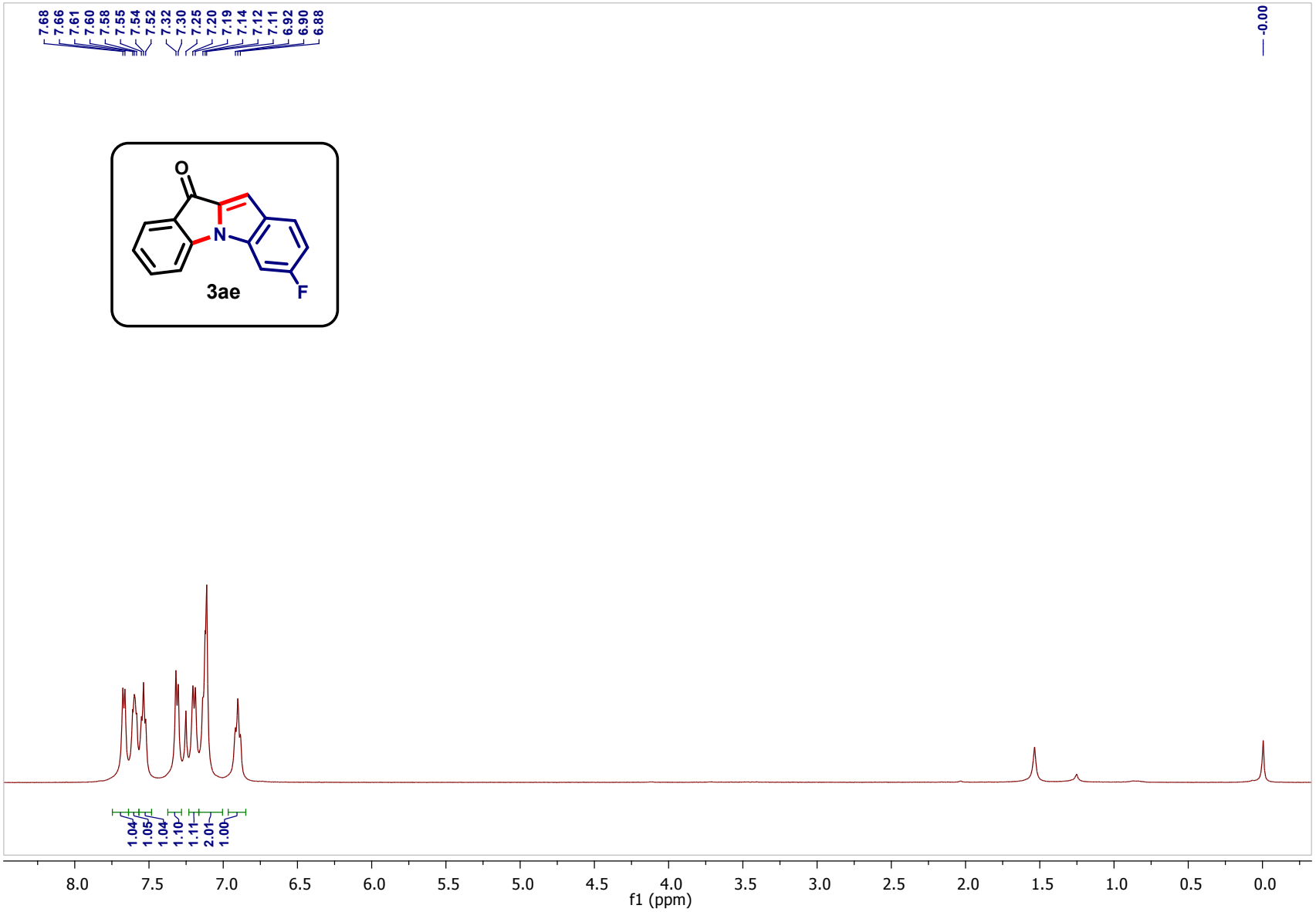
135.65
133.06
132.98
130.91
129.06
125.36
124.10
116.89
116.68
112.08
112.01
111.02
109.88
109.69
107.40
107.36
77.25
77.00
76.75
O
N
F
3ad
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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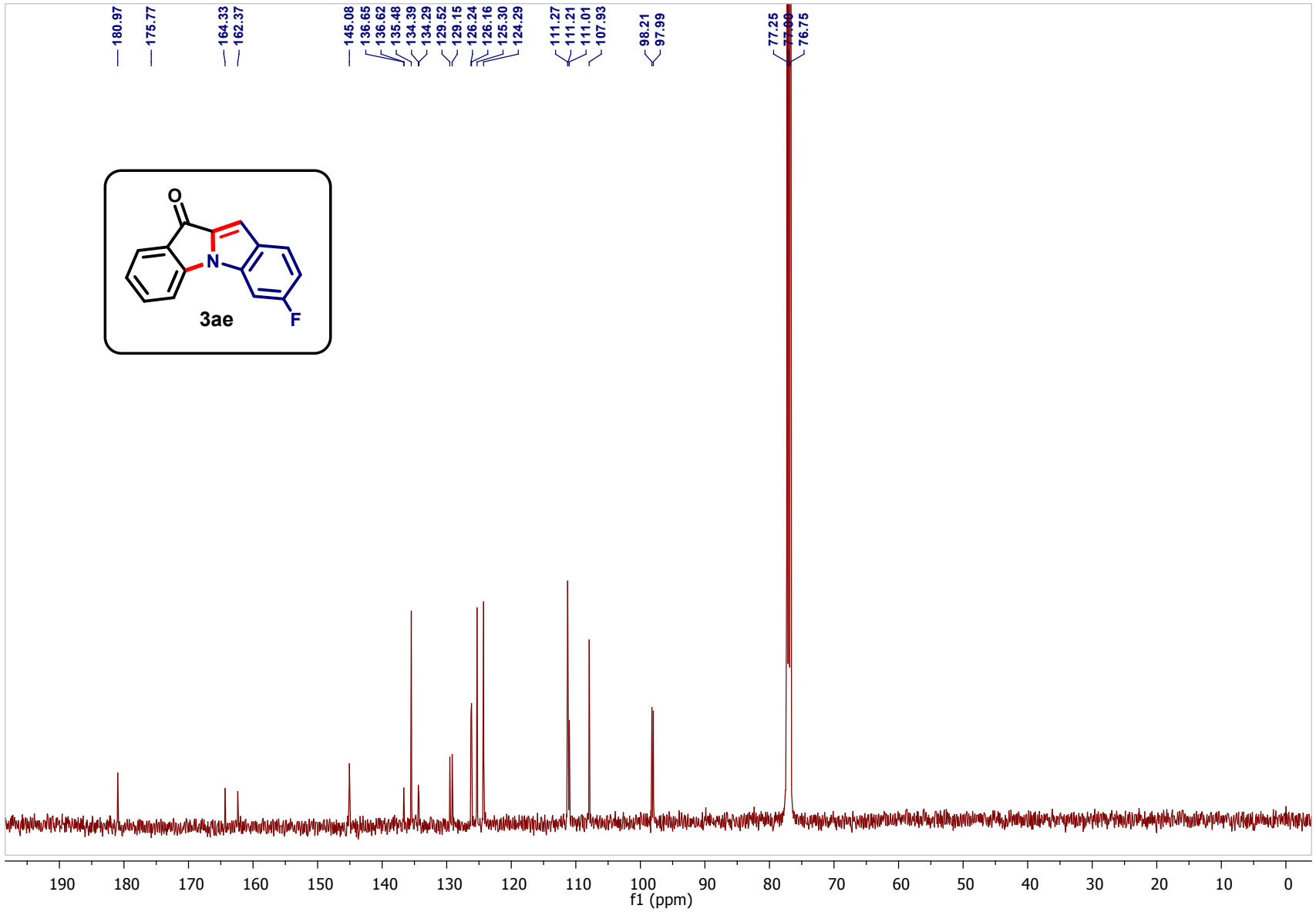
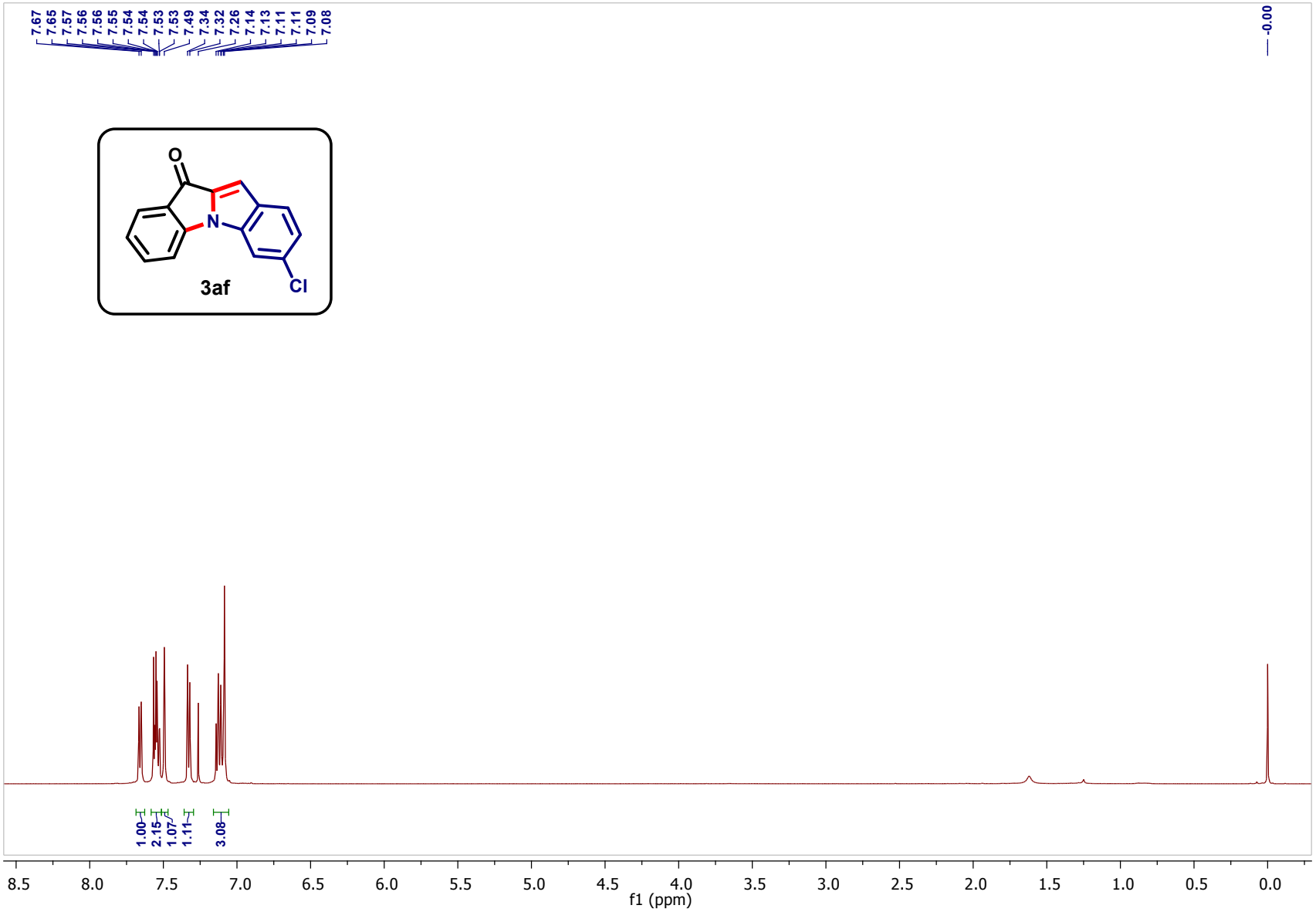
7.66
7.61
7.60
7.58
7.55
7.54
7.52
7.32
7.30
7.25
7.20
7.19
7.14
7.12
7.11
6.92
6.90
6.88
-0.00
O
N
F
3ae
1.04
1.05
1.04
1.10
1.11
2.01
1.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


180.97
175.77
164.33
162.37
145.08
136.65
136.62
135.48
134.39
134.29
129.52
129.15
126.24
126.16
125.30
124.29
111.27
111.21
111.01
107.93
98.21
97.99
77.25
77.00
76.75
O
N
F
3ae
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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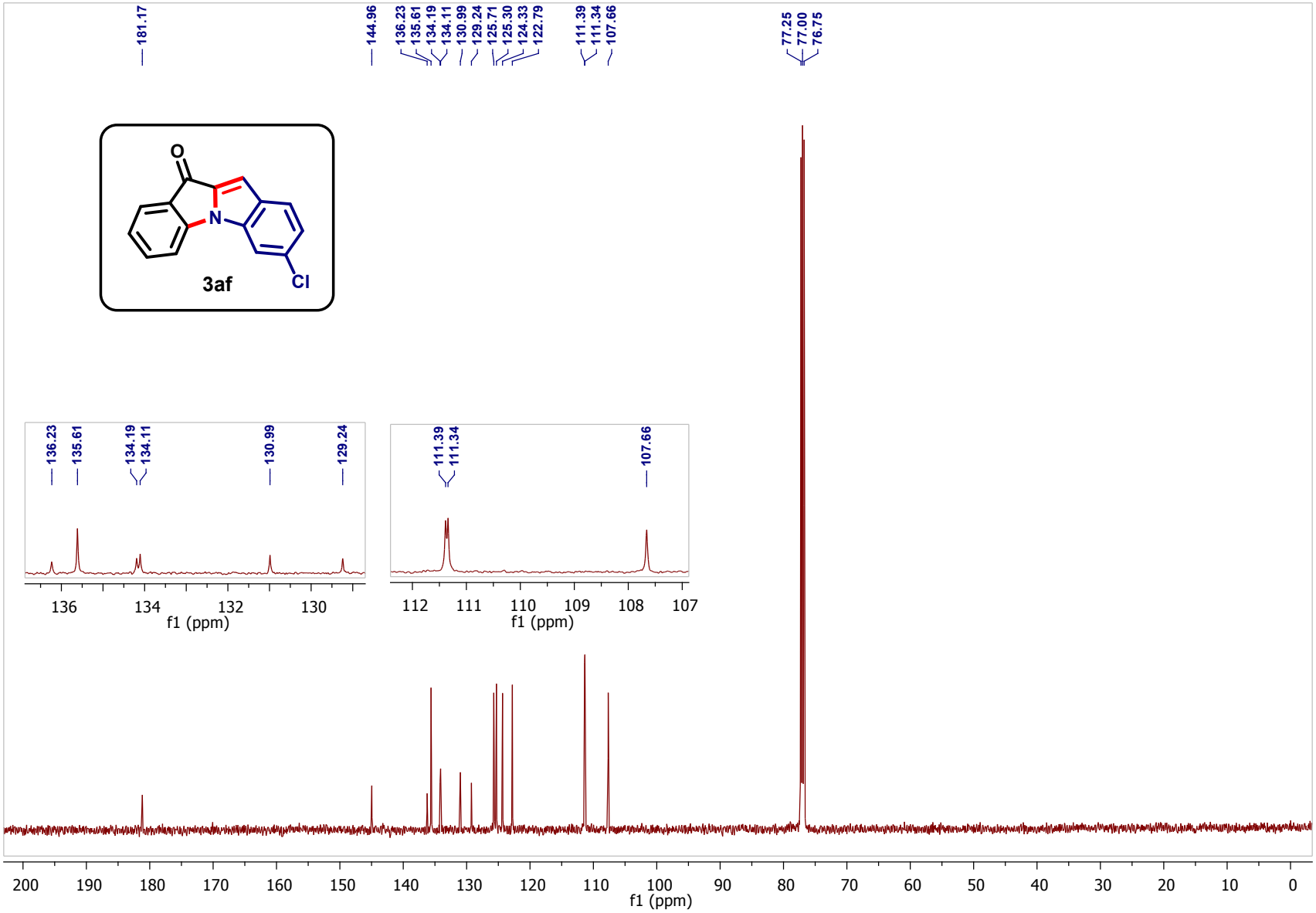
7.65
7.57
7.56
7.56
7.55
7.54
7.54
7.53
7.53
7.49
7.34
7.32
7.26
7.14
7.13
7.11
7.11
7.09
7.08
-0.00
O
N
Cl
3af
1.00
2.15
1.07
1.11
3.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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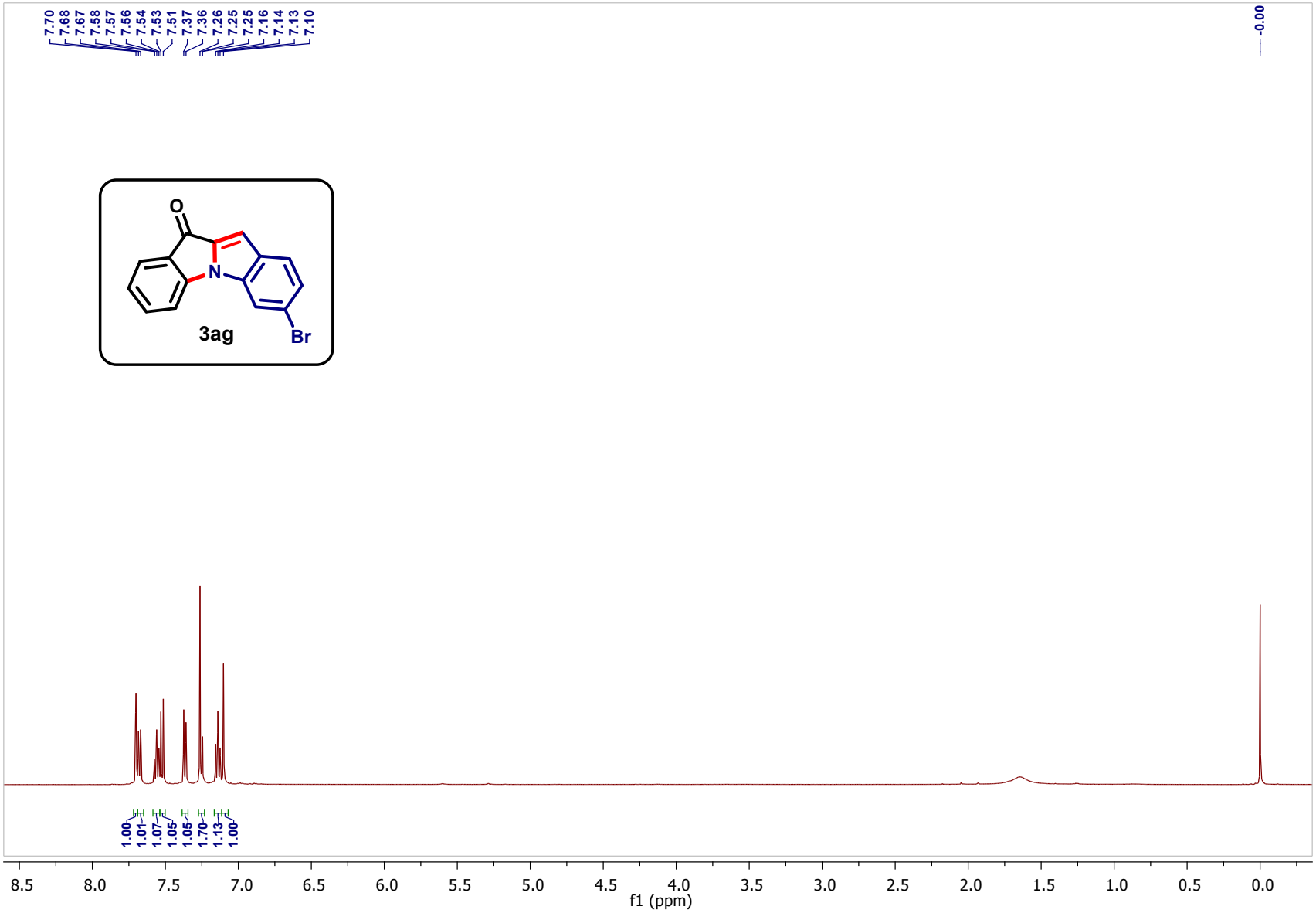
144.96
136.23
135.61
134.19
134.11
130.99
129.24
125.71
125.30
124.33
122.79
111.39
111.34
107.66
77.25
77.00
76.75
O
N
Cl
3af
136.23
135.61
134.19
134.11
130.99
129.24
136
134
132
130
f1 (ppm)
111.39
111.34
107.66
112
111
110
109
108
107
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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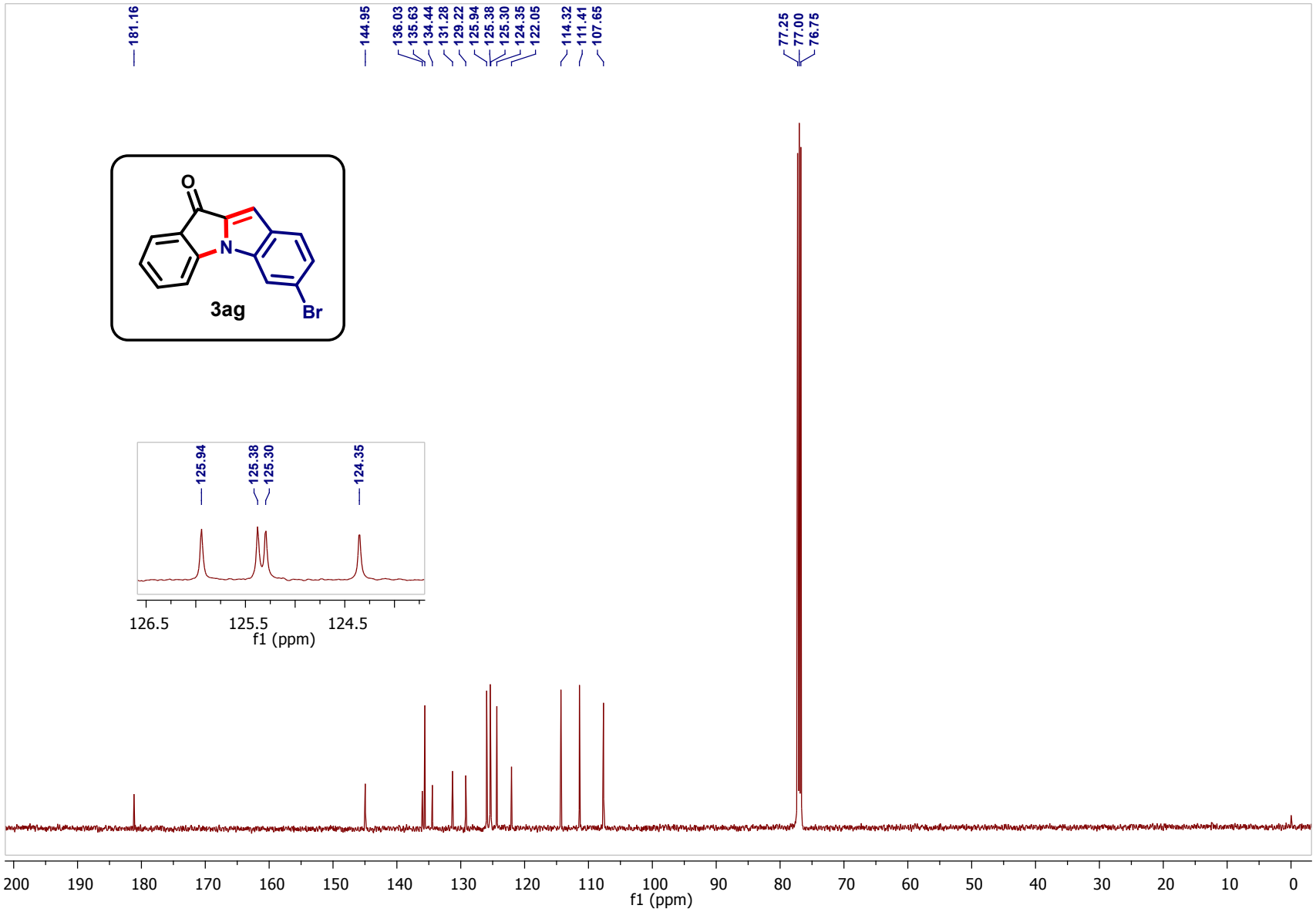
7.56
7.54
7.53
7.51
7.37
7.36
7.26
7.25
7.16
7.14
7.13
7.10
-0.00
O
N
Br
3ag
1.00
1.01
1.07
1.05
1.05
1.70
1.13
1.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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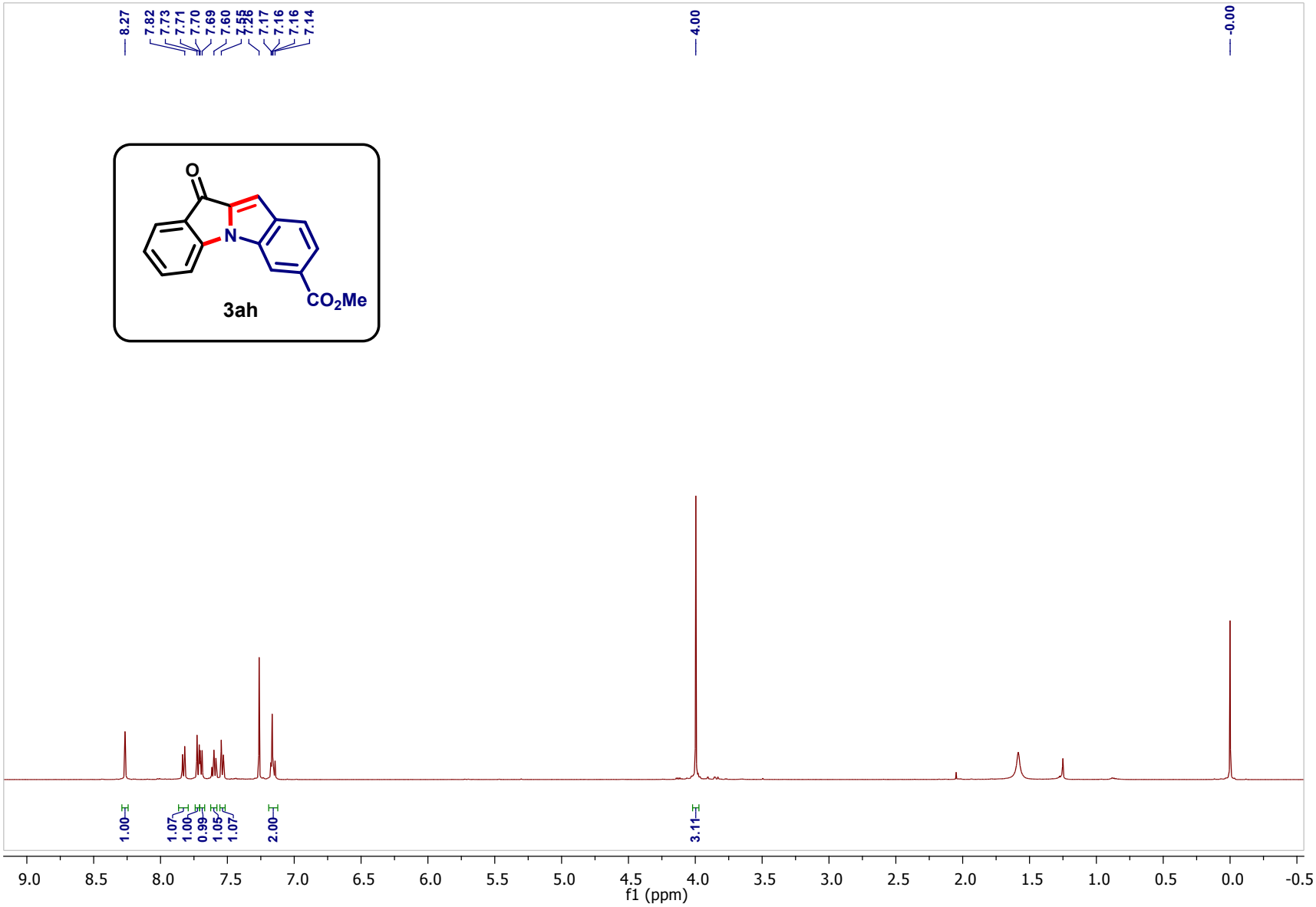
135.63
134.44
131.28
129.22
125.94
125.38
125.30
124.35
122.05
114.32
111.41
107.65
77.25
77.00
76.75
O
N
Br
3ag
125.94
125.38
125.30
124.35
126.5
125.5
124.5
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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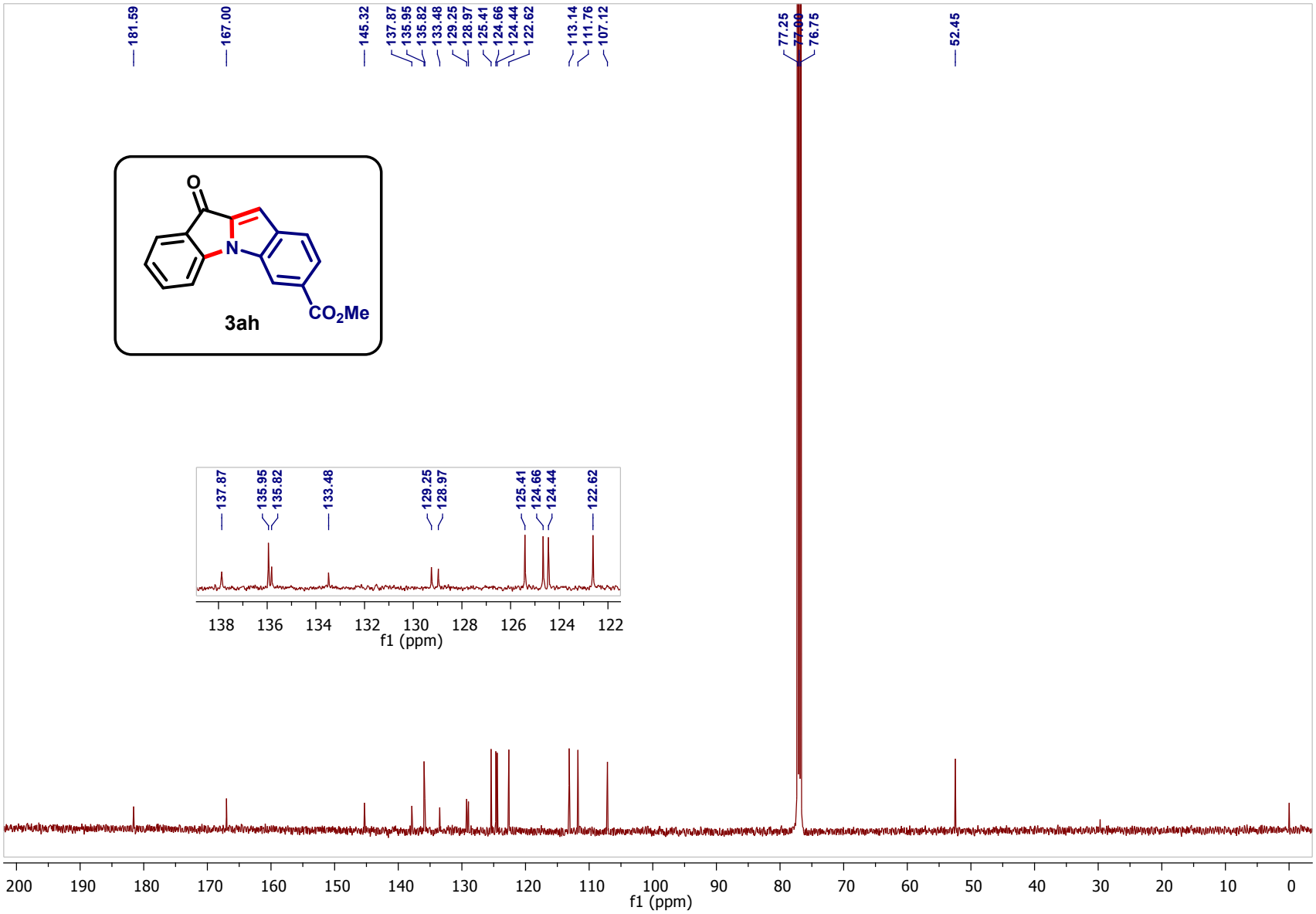
7.82
7.73
7.71
7.70
7.69
7.60
7.55
7.28
7.17
7.16
7.16
7.14
4.00
-0.00
O
N
CO2Me
3ah
1.00
1.07
1.00
0.99
1.05
1.07
2.00
3.11
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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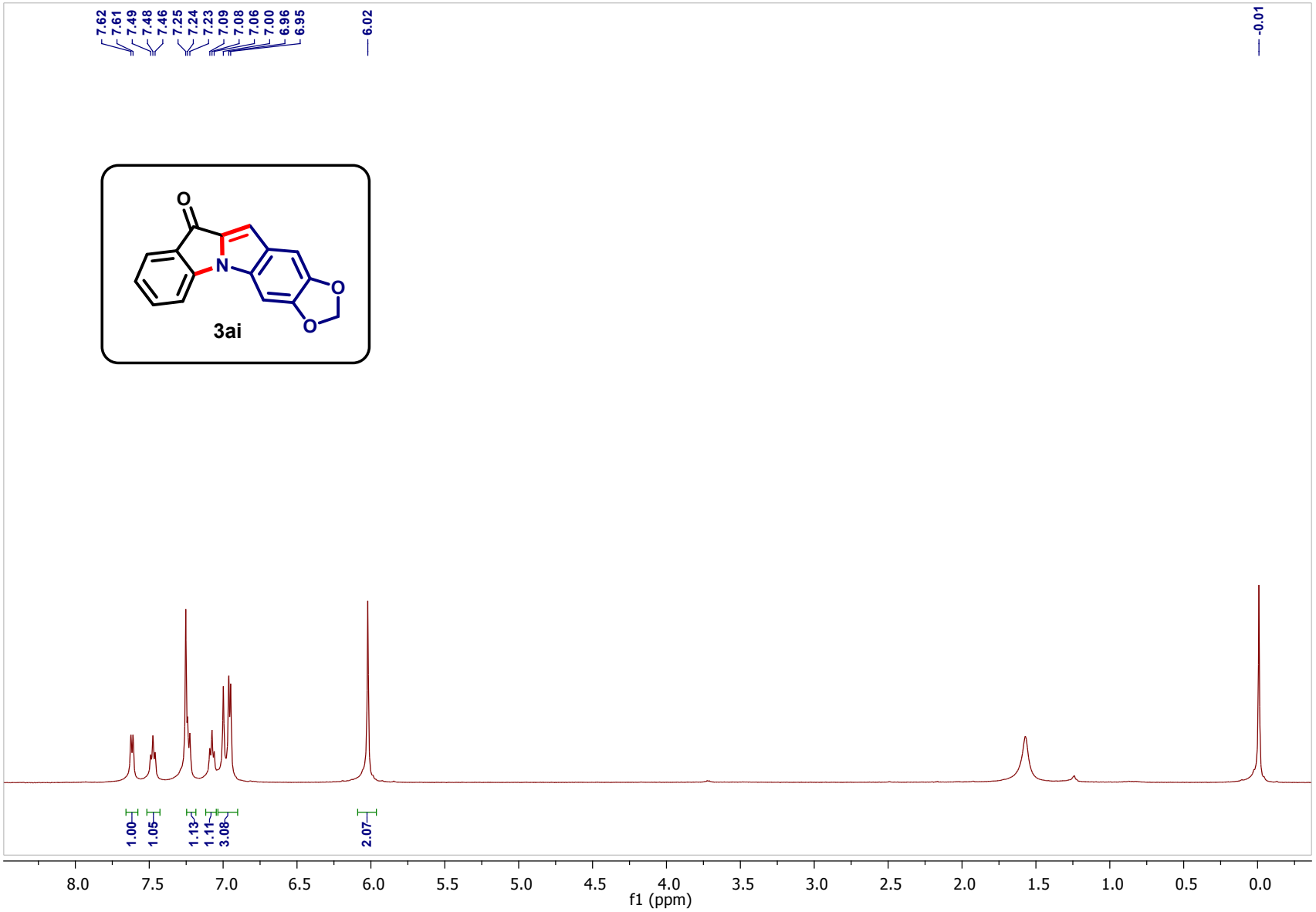
133.48
129.25
128.97
125.41
124.66
124.44
122.62
113.14
111.76
107.12
77.25
77.00
76.75
52.45
O
N
CO2Me
3ah
f1 (ppm)
f1 (ppm)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7.61
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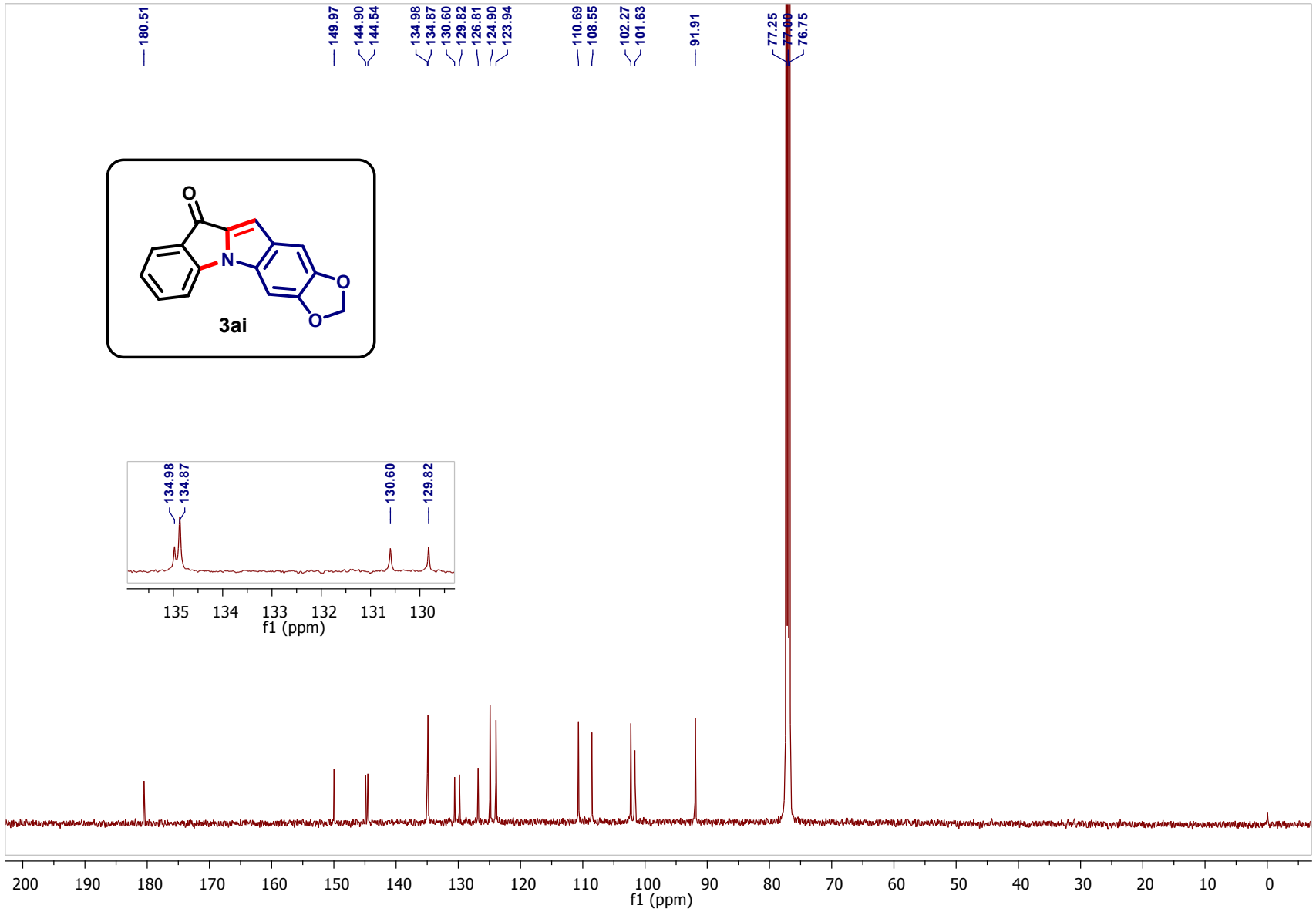
7.48
7.46
7.25
7.24
7.23
7.09
7.08
7.06
7.00
6.96
6.95
6.02
-0.01
O
N
O
O
3ai
1.00
1.05
1.13
1.11
3.08
2.07
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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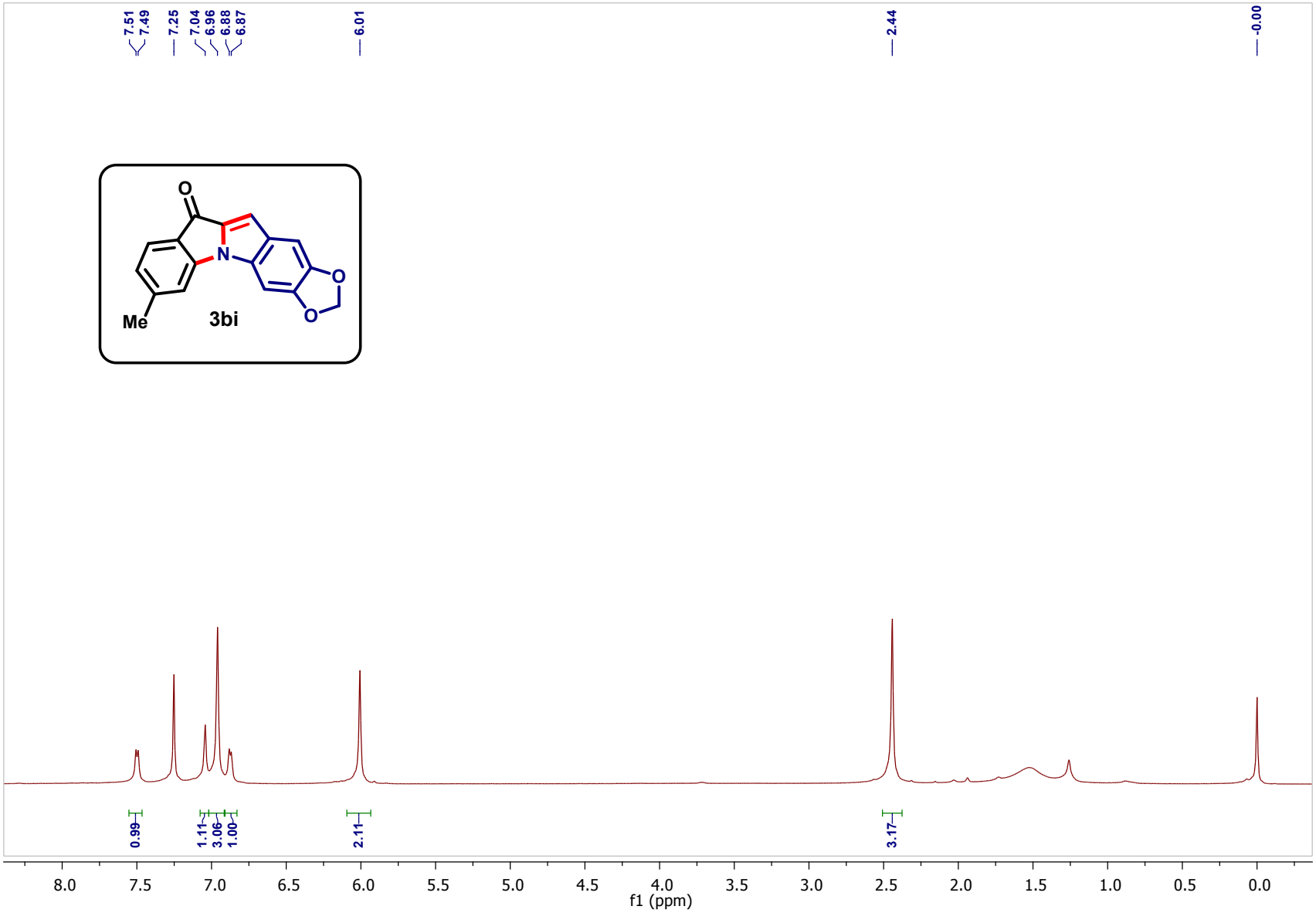
144.54
134.98
134.87
130.60
129.82
126.81
124.90
123.94
110.69
108.55
102.27
101.63
91.91
77.25
77.00
76.75
O
N
O
O
3ai
134.98
134.87
130.60
129.82
135
134
133
132
131
130
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.49
7.25
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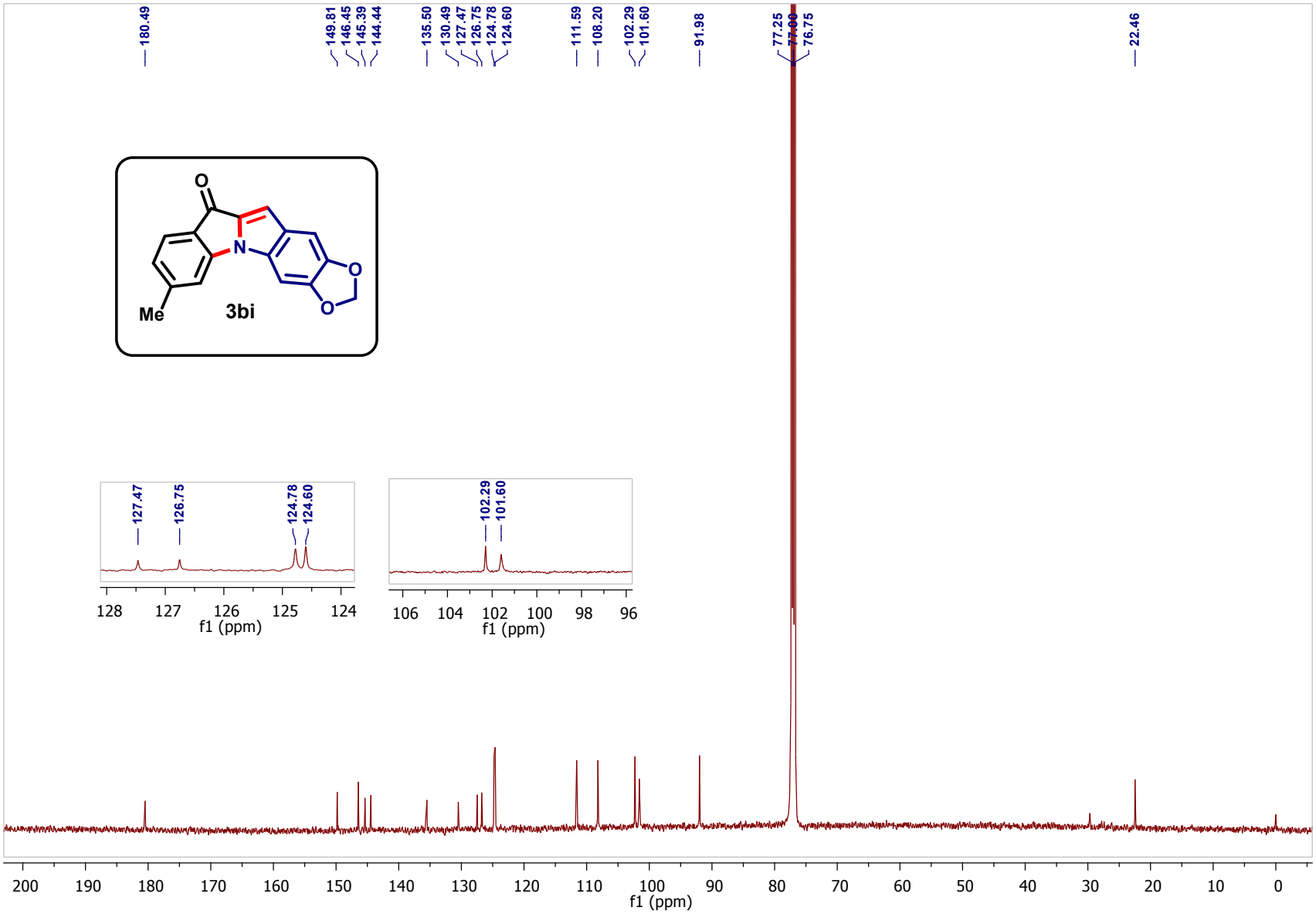
6.96
6.88
6.87
6.01
2.44
-0.00
O
N
O
O
Me
3bi
0.99
1.11
3.06
1.00
2.11
3.17
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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145.39
144.44
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127.47
126.75
124.78
124.60
111.59
108.20
102.29
101.60
91.98
77.25
77.00
76.75
22.46
O
N
O
O
Me
3bi
127.47
126.75
124.78
124.60
128
127
126
125
124
f1 (ppm)
102.29
101.60
106
104
102
100
98
96
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)