Electronic Supplementary Information

P/N-Heteroleptic Cu(I)-photosensitizer-catalyzed domino radical relay annulation of 1,6-enynes with aryldiazonium salts

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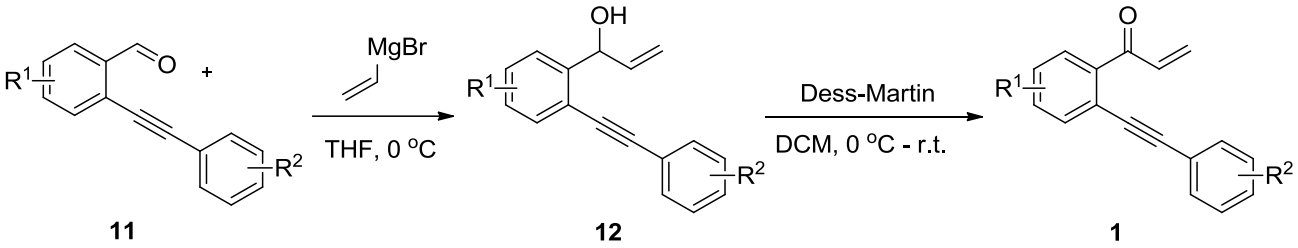
Contents

1. General information

All glassware was thoroughly oven-dried. Solvents were dried according to standard methods prior to use. All commercially available reagents were obtained from chemical suppliers and used after proper purification if necessary. Thin-layer chromatography (TLC) plates were visualized by exposure to ultraviolet light. Flash chromatography was carried out using silica gel (100-200 mesh). Melting points are uncorrected. NMR spectra were recorded with tetramethylsilane as the internal standard. ^{1}H NMR and ^{13}C NMR spectra of $CDCl_3$ solutions were recorded at 500 and 125 MHz (Bruker Avance), respectively and resonances (δ) are given in parts per million relatives to tetramethylsilane. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), mul-tiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet), integration, coupling constant (Hz) and assignment. Data for ^{13}C NMR are reported as chemical shift. GC-MS experiments were performed with an Agilent 6890N GC system equipped with a 5973N mass-selective detector with EI source; High resolution mass spectra (HRMS) were obtained on a TOF MS instrument with EI or ESI source.

2. General procedure for the preparation of the starting material 1[1,2]



General procedure: Vinyl magnesium bromide (1.2 mmol, 1.2 equiv.) was added dropwise to a solution of *ortho*-phenylethynylbenzaldehyde **11**[1] (1.0 mmol, 1 equiv.) in anhydrous THF (0.35 M) at 0 ˚C for 30 min and then stirred at rt for 6 h. The reaction was quenched with aq. NH_4Cl and the organic layers was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine (3 × 10 mL), dried over $MgSO_4$, and concentrated under reduced pressure to give crude **12**.[2] Crude **12** was used for the next step without further purification.

To a solution of compound **12** (1.0 mmol, 1 equiv.) in DCM was added Dess-Martin

reagent (1.2 mmol, 1.2 equiv.) at 0 ˚C while stirring. The resulting mixture was then stirred at rt. Upon complete consumption of the starting material as monitored by TLC, the reaction mixture was quenched with saturated aqueous $Na_2S_2O_3$ and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with brine, and dried over anhydrous Na_2SO_4. The solvent was evaporated under vacuum and the crude product were purified by column chromatography on silica gel (100-200 mesh), eluting with the indicated mixture of EA/PE (1:10 (v/v)) to give compound **1**.

3. Preparation of the starting material aryldiazonium tetrafluoroborates 2 and safety notice of handling 2

All aryldiazonium tetrafluoroborates (**2**) were synthesized from the corresponding anilines according to the literature procedure and their analytical data are consistent with the reported ones.[3]

Safety notice of handling 2. Some aryldiazonium tetrafluoroborates could be explosive and should be handled carefully. Face shields, leather gloves, and protective leather clothing are highly recommended when handling these compounds.

4. Preparation of the photosensitizers (*PS 1-PS 5*)

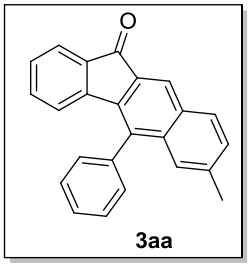
The photosensitizers ***PS 1-PS5*** were synthesized according to the literature procedure and their analytical data are consistent with the reported ones.[4]

5. General procedure for the synthesis of products 3 and characterization

Typical procedure: 4-methylphenyldiazonium tetrafluorborate **2a** (1.2 mmol, 247.1 mg, 3 equiv. based on **1a**), ***PS 1*** (23.0 mg, 5 mol % based on **1a**) and $CuSO_4 \cdot 5H_2O$ (10.0 mg, 10 mol % based on **1a**) were placed in a 25 mL Schlenk tube. The tube was evacuated and refilled with N_2 three times. 1-(2-(phenylethynyl)phenyl)prop-2-en-1-one **1a** (92.9 mg, 0.4 mmol) and EtOH (4 mL) were added, and the resulting mixture was irradiated with a blue LED lamp (15 W) at 40 ˚C under N_2 atmosphere for 4 h. Upon completion, the reaction mixture was evaporated and purified by column chromatography on silica gel (100-200 mesh), eluting with the indicated mixture of EA/PE (1:20 (v/v)) to give the pure product **3aa**.

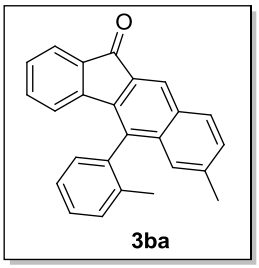
Characterization of the products

7-methyl-5-phenyl-11*H*-benzo[*b*]fluoren-11-one (3aa)



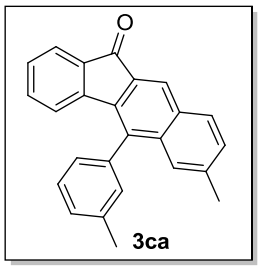
Yellow solid (66.5 mg, 52%). m.p. 159–161 ˚C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 (s, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.75–7.70 (m, 1H), 7.66–7.59 (m, 3H), 7.44–7.38 (m, 2H), 7.33–7.28 (m, 1H), 7.24–7.15 (m, 3H), 6.29 (d, *J* = 7.3 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.2, 145.1, 139.3, 137.6, 137.1, 136.6, 135.48, 134.53, 134.1, 131.8, 131.5, 130.6, 129.7, 129.2, 128.9, 128.5, 128.2, 126.4, 125.1, 124.1, 123.7, 22.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{17}O$ 321.1279; Found 321.1277.

7-methyl-5-(*o*-tolyl)-11*H*-benzo[*b*]fluoren-11-one (3ba)



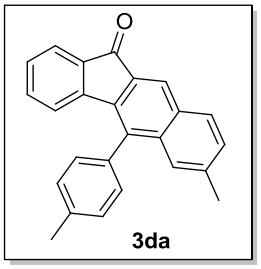
Yellow solid (70.9 mg, 53%). m.p. 146–147 ˚C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.22 (s, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.76–7.72 (m, 1H), 7.55–7.46 (m, 2H), 7.46–7.40 (m, 1H), 7.33 (dd, J_1 = 8.2 Hz, J_2 = 1.4 Hz, 1H), 7.27–7.17 (m, 3H), 7.13 (d, *J* = 0.6 Hz, 1H), 6.21 (d, *J* = 7.1 Hz, 1H), 2.40 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.3, 145.2, 139.5, 137.0, 136.8, 136.7, 136.54, 135.51, 134.9, 133.4, 131.9, 131.7, 130.8, 130.6, 129.8, 129.0, 128.6, 128.6, 126.8, 125.9, 125.0, 124.1, 123.2, 22.1, 19.6. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{18}ONa$ 357.1255; Found 357.1263.

7-methyl-5-(*m*-tolyl)-11*H*-benzo[*b*]fluoren-11-one (3ca)



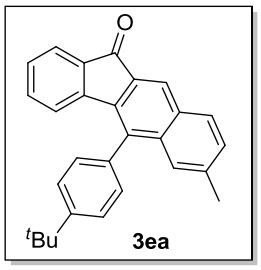
Yellow solid (64.2 mg, 48%). m.p. 142–144 ˚C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 (s, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.76–7.71 (m, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 7.7 Hz, 1H), 7.31 (dd, J_1 = 8.2 Hz, J_2 = 1.4 Hz, 1H), 7.26–7.18 (m, 5H), 6.33 (dd, J_1 = 6.4 Hz, J_2 = 1.4 Hz, 1H), 2.49 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.3, 145.2, 139.3, 138.9, 137.5, 137.1, 136.6, 135.4, 134.6, 134.3, 131.8, 131.5, 130.6, 130.3, 129.1, 128.9, 128.9, 128.4, 126.7, 126.5, 125.0, 124.0, 123.8, 22.1, 21.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{19}O$ 335.1436; Found 335.1439.

7-methyl-5-(*p*-tolyl)-11*H*-benzo[*b*]fluoren-11-one (3da)



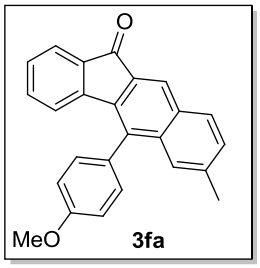
Yellow solid (68.2 mg, 51%). m.p. 179–180 ˚C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 (s, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.76–7.70 (m, 1H), 7.43 (d, *J* = 7.7 Hz, 2H), 7.33–7.28 (m, 3H), 7.24 (s, 1H), 7.23–7.18 (m, 2H), 6.38 (d, *J* = 6.5 Hz, 1H), 2.57 (s, 3H), 2.40 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$): δ 193.4, 145.3, 139.3, 137.9, 137.3, 136.6, 135.6, 134.6, 134.4, 134.3, 131.8, 131.6, 130.6, 130.0, 129.6, 128.9, 128.5, 126.5, 125.0, 124.1, 123.8, 22.1, 21.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{19}O$ 335.1436; Found 335.1440.

5-(4-(*tert*-butyl)phenyl)-7-methyl-11*H*-benzo[*b*]fluoren-11-one (3ea)



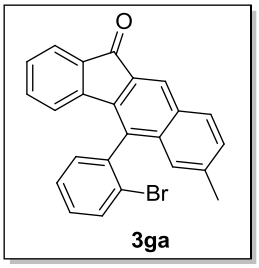
Yellow solid (64.8 mg, 43%). m.p. 224–226 ˚C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.20 (s, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.74–7.71 (m, 1H), 7.65–7.61 (m, 2H), 7.35–7.30 (m, 3H), 7.27 (d, *J* = 0.6 Hz, 1H), 7.24–7.15 (m, 2H), 6.26 (d, *J* = 7.5 Hz, 1H), 2.41 (s, 3H), 1.50 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.4, 151.3, 145.3, 139.3, 137.3, 136.6, 135.7, 134.6, 134.4, 131.8, 131.5, 130.6, 129.3, 128.9, 128.4, 126.5, 126.1, 125.0, 124.1, 123.8, 34.9, 31.5, 22.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{25}O$ 377.1905; Found 377.1903.

5-(4-methoxyphenyl)-7-methyl-11*H*-benzo[*b*]fluoren-11-one (3fa)



Yellow solid (42.3 mg, 37%). m.p. 174–176 ˚C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (s, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.75–7.69 (m, 1H), 7.32–7.28 (m, 3H), 7.25 (s, 1H), 7.23–7.20 (m, 2H), 7.17–7.13 (m, 2H), 6.43–6.39 (m, 1H), 3.98 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.3, 159.5, 145.3, 139.3, 137.5, 136.6, 135.8, 134.5, 133.9, 131.8, 131.5, 130.9, 130.6, 129.5, 128.8, 128.4, 126.4, 124.9, 124.0, 123.8, 114.6, 55.4, 22.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{19}O_2$ 351.1385; Found 351.1391.

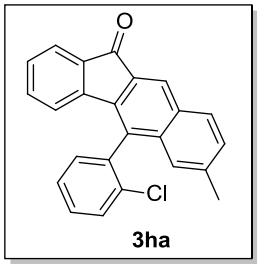
5-(2-bromophenyl)-7-methyl-11*H*-benzo[*b*]fluoren-11-one (3ga)



Yellow solid (103.7 mg, 65%). m.p. 232–234 ˚C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.25 (s, 1H), 7.91–7.86 (m, 2H), 7.77–7.74 (m, 1H), 7.58 (m, 1H), 7.50 (m, 1H), 7.40 (dd, J_1 = 7.5, J_2 = 1.7 Hz, 1H), 7.34 (dd, J_1 = 8.2 Hz, J_2 = 1.4 Hz, 1H), 7.2757.21 (m, 2H), 7.09 (d, J_1 = 0.6 Hz, 1H), 6.27 (dd, J_1 = 6.6 Hz, J_2 = 1.0 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.0, 144.7, 139.7, 138.4, 136.6, 136.2, 135.9, 134.9, 133.5, 132.6,

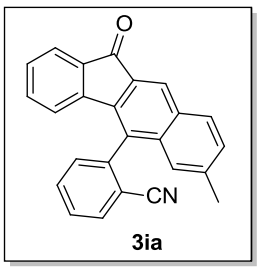
131.8, 131.61, 131.60, 130.8, 130.1, 129.1, 128.8, 128.3, 125.7, 125.54, 124.45, 124.2, 123.1, 22.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{16}OBr$ 399.0385; Found 399.0377.

5-(2-chlorophenyl)-7-methyl-11*H*-benzo[*b*]fluoren-11-one (3ha)



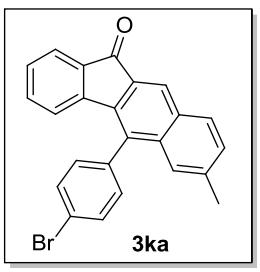
Yellow solid (76.6 mg, 54%). m.p. 224–226 ˚C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.25 (s, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 7.1 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.61–7.56 (m, 1H), 7.55–7.50 (m, 1H), 7.41 (d, *J* = 7.4 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.28–7.21 (m, 2H), 7.10 (s, 1H), 6.28 (d, *J* = 7.0 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.0, 144.7, 139.7, 136.6, 136.31, 136.29, 136.1, 134.9, 134.4, 131.8, 131.7, 131.6, 130.8, 130.3, 130.0, 129.1, 128.8, 127.7, 125.7, 125.6, 124.2, 123.0, 22.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{16}OCl$ 355.0890; Found 355.0890.

2-(7-methyl-11-oxo-11*H*-benzo[*b*]fluoren-5-yl)benzonitrile (3ia)



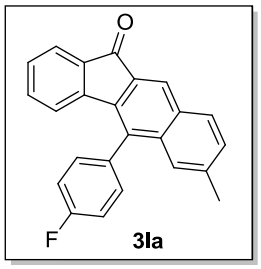
Yellow solid (77.4 mg, 56%). m.p. 273–274 ˚C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.28 (s, 1H), 8.00 (dd, J_1 = 7.8 Hz, J_2 = 0.8 Hz, 1H), 7.91–7.85 (m, 2H), 7.81–7.71 (m, 2H), 7.58 (dd, J_1 = 7.7 Hz, J_2 = 0.6 Hz, 1H), 7.36 (dd, J_1 = 8.2 Hz, J_2 = 1.3 Hz, 1H), 7.31–7.24 (m, 1H), 7.24–7.17 (m, 1H), 7.00 (d, *J* = 0.7 Hz, 1H), 6.12 (d, *J* = 7.6 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.6, 144.2, 141.8, 140.1, 136.7, 136.5, 136.2, 134.7, 133.8, 133.6, 131.7, 131.7, 131.3, 131.0, 129.4, 129.3, 129.2, 129.1, 126.3, 125.3, 124.5, 122.8, 117.1, 114.1, 22.1. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{15}NO$ 368.1051; Found 368.1050.

5-(4-bromophenyl)-7-methyl-11*H*-benzo[*b*]fluoren-11-one (3ka)



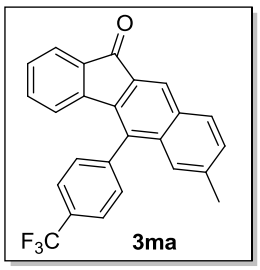
Yellow solid (100.6 mg, 63%). m.p. 229–230 ˚C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 (s, 1H), 7.87–7.70 (m, 4H), 7.34–7.29 (m, 3H), 7.27–7.23 (m, 2H), 7.15 (s, 1H), 6.42–6.36 (m, 1H), 2.41 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.0, 144.8, 139.6, 136.8, 136.6, 135.6, 134.7, 132.6, 131.8, 131.63, 131.5, 130.7, 129.1, 128.8, 126.1, 125.4, 124.3, 123.6, 122.5, 22.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{15}ONaBr$ 421.0206; Found 421.0204.

5-(4-fluorophenyl)-7-methyl-11*H*-benzo[*b*]fluoren-11-one (3la)



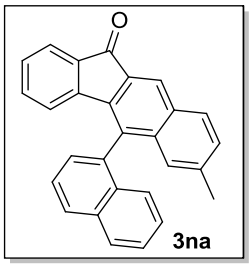
Yellow solid (81.2 mg, 60%). m.p. 209–211 ˚C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 (s, 1H), 7.83 (d, J = 8.2 Hz, 1H), 7.75–7.71 (m, 1H), 7.41–7.30 (m, 5H), 7.26–7.20 (m, 2H), 7.17 (s, 1H), 6.33 (dd, J_1 = 6.1 Hz, J_2 = 2.3 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 193.0, 162.8 (d, J = 247.5 Hz), 144.9, 139.5, 137.1, 136.6, 135.8, 134.6, 133.4 (d, J = 3.5 Hz), 132.9, 131.7, 131.5 (d, J = 7.7 Hz), 131.5, 130.7, 129.0, 128.7, 126.2, 125.3, 124.2, 123.6, 116.4 (d, J = 21.3 Hz), 22.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{16}OF$ 339.1185; Found 339.1180.

7-methyl-5-(4-(trifluoromethyl)phenyl)-11*H*-benzo[*b*]fluoren-11-one (3ma)



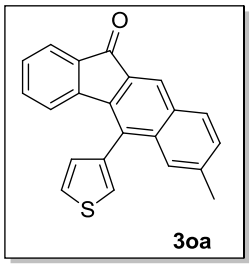
Yellow solid (105.6 mg, 68%). m.p. 209–211 ˚C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17 (d, J = 3.5 Hz, 1H), 7.91 (d, J = 8.0 Hz, 2H), 7.82 (dd, J_1 = 8.2 Hz, J_2 = 2.6 Hz, 1H), 7.74–7.69 (m, 1H), 7.57 (d, J = 7.8 Hz, 2H), 7.32 (d, J = 8.2 Hz, 1H), 7.26–7.19 (m, 2H), 7.09 (s, 1H), 6.28–6.23 (m, 1H), 2.41 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.7, 144.5, 141.7, 139.8, 136.6, 136.5, 135.5, 134.7, 132.2, 131.7, 131.5, 130.8, 130.6 (q, J = 32.5 Hz), 130.4, 129.1, 128.9, 126.3 (q, J = 3.7 Hz), 125.9, 125.5, 124.3, 124.2 (q, J = 272.3 Hz), 123.4, 22.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{16}OF_3$ 389.1159; Found 389.1153.

7-methyl-5-(naphthalen-1-yl)-11*H*-benzo[*b*]fluoren-11-one (3na)



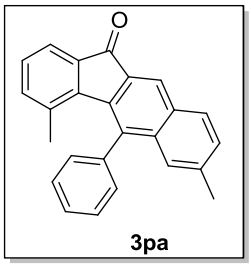
Yellow solid (69.6 mg, 47%). m.p. 215–217 ˚C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.31 (s, 1H), 8.13 (d, J = 8.3 Hz, 1H), 8.05 (d, J = 8.3 Hz, 1H), 7.91 (d, J = 8.2 Hz, 1H), 7.75–7.69 (m, 2H), 7.57–7.50 (m, 2H), 7.43 (d, J = 8.4 Hz, 1H), 7.35–7.29 (m, 2H), 7.17–7.12 (m, 1H), 7.03 (s, 1H), 7.01–6.95 (m, 1H), 5.84 (d, J = 7.7 Hz, 1H), 2.28 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.3, 144.8, 139.6, 137.6, 136.7, 136.6, 135.1, 134.7, 133.9, 132.3, 131.6, 130.7, 129.1, 128.7, 128.5, 128.4, 127.7, 126.7, 126.48, 126.46, 126.1, 125.7, 125.4, 124.0, 123.6, 22.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{19}O$ 371.1436; Found 371.1430.

7-methyl-5-(thiophen-3-yl)-11*H*-benzo[b]fluoren-11-one (3oa)



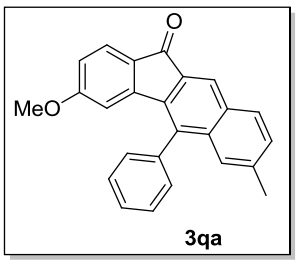
Yellow solid (57.4 mg, 44%). m.p. 201–202 ˚C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 (s, 1H), 7.84 (d, J = 8.2 Hz, 1H), 7.76–7.71 (m, 1H), 7.69–7.64 (m, 1H), 7.38–7.35 (m, 1H), 7.34–7.29 (m, 2H), 7.29–7.23 (m, 2H), 7.16 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 6.47–6.41 (m, 1H), 2.43 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.2, 145.0, 139.5, 137.5, 137.2, 136.51, 136.46, 134.7, 131.8, 131.4, 130.6, 129.1, 128.99, 128.95, 128.7, 126.9, 126.2, 125.3, 124.2, 124.1, 123.5, 22.1. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{14}ONaS$ 349.0663; Found 349.0660.

4,7-dimethyl-5-phenyl-11*H*-benzo[*b*]fluoren-11-one (3pa)



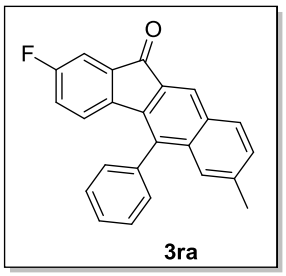
Yellow solid (82.8 mg, 62%). m.p. 218–219 ˚C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.25 (s, 1H), 7.82 (d, J = 8.2 Hz, 1H), 7.67 (dd, J_1 = 7.2 Hz, J_2 = 0.6 Hz, 1H), 7.56–7.50 (m, 3H), 7.48–7.43 (m, 2H), 7.36 (d, J = 0.7 Hz, 1H), 7.31 (dd, J_1 = 8.2 Hz, J_2 = 1.3 Hz, 1H), 7.19 (t, J = 7.4 Hz, 1H), 7.11 (dd, J_1 = 7.5, J_2 = 0.5 Hz, 1H), 2.39 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.2, 144.6, 140.1, 139.2, 139.0, 138.2, 137.9, 137.4, 135.6, 134.7, 133.1, 131.8, 131.1, 130.4, 128.9, 128.64, 128.4, 128.0, 127.1, 125.2, 121.9, 22.3, 21.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{19}O$ 335.1436; Found 335.1431.

3-methoxy-7-methyl-5-phenyl-11*H*-benzo[*b*]fluoren-11-one (3qa)



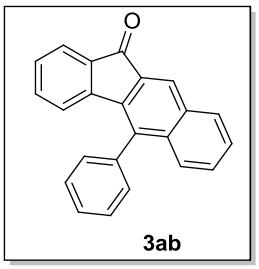
Yellow solid (72.8 mg, 52%). m.p. 169–170 ˚C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15 (s, 1H), 7.84 (d, J = 8.2 Hz, 1H), 7.68–7.57 (m, 4H), 7.46–7.41 (m, 2H), 7.34–7.30 (m, 1H), 7.24 (s, 1H), 6.70 (dd, J_1 = 8.3 Hz, J_2 = 2.2 Hz, 1H), 5.77 (d, J = 2.2 Hz, 1H), 3.53 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 191.8, 164.8, 147.7, 139.0, 137.5, 136.7, 134.8, 133.9, 132.8, 131.7, 130.5, 129.9, 129.8, 129.2, 128.9, 128.2, 126.4, 125.8, 124.3, 114.7, 108.6, 55.1, 22.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{19}O_2$ 351.1385; Found 351.1388.

2-fluoro-7-methyl-5-phenyl-11*H*-benzo[*b*]fluoren-11-one (3ra)



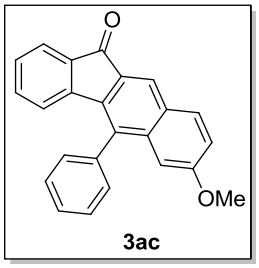
Yellow solid (78.4 mg, 58%). m.p. 206–208 ˚C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 (s, 1H), 7.83 (d, J = 8.2 Hz, 1H), 7.66–7.59 (m, 3H), 7.43–7.36 (m, 3H), 7.32 (dd, J_1 = 8.2 Hz, J_2 = 1.3 Hz, 1H), 7.20 (s, 1H), 6.86 (td, J_1 = 8.7, J_2 = 2.6 Hz, 1H), 6.23–6.19 (m, 1H), 2.40 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 192.0 (d, J = 2.2 Hz), 163.1 (d, J = 250.4 Hz), 141.0 (d, J = 2.7 Hz), 139.7, 138.7 (d, J = 7.2 Hz), 137.4, 137.2, 134.8, 133.7 (d, J = 1.4 Hz), 131.9 (d, J = 1.7 Hz), 131.2, 130.7, 129.7, 129.4, 129.0, 128.4, 126.4, 125.5, 125.1 (d, J = 7.7 Hz), 121.1 (d, J = 22.9 Hz), 111.1 (d, J = 23.0 Hz), 22.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{16}OF$ 339.1185; Found 339.1180.

5-phenyl-11*H*-benzo[*b*]fluoren-11-one (3ab)



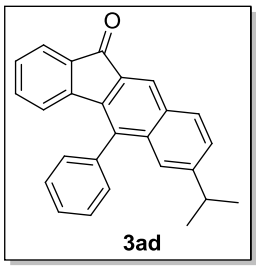
Yellow solid (84.2 mg, 55%). m.p. 230–232 ˚C (lit.[5] m.p. 232 ˚C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.24 (s, 1H), 7.94 (d, J = 7.3 Hz, 1H), 7.74 (d, J = 7.0 Hz, 1H), 7.65–7.59 (m, 3H), 7.50–7.40 (m, 5H), 7.25–7.17 (m, 2H), 6.35 (d, J = 7.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.2, 145.1, 137.4, 136.9, 136.5, 135.3, 134.7, 134.6, 133.4, 132.5, 130.8, 129.7, 129.3, 128.9, 128.6, 128.3, 127.1, 126.8, 125.2, 124.2, 123.8.

7-methoxy-5-phenyl-11*H*-benzo[*b*]fluoren-11-one (3ac)



Yellow solid (65.8 mg, 49%). m.p. 126–127 ˚C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (s, 1H), 7.84 (d, J = 8.9 Hz, 1H), 7.74–7.70 (m, 1H), 7.65–7.58 (m, 3H), 7.45–7.39 (m, 2H), 7.25–7.10 (m, 3H), 6.77 (d, J = 2.4 Hz, 1H), 6.30 (d, J = 7.5 Hz, 1H), 3.72 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.1, 160.2, 145.0, 138.7, 137.6, 136.7, 136.2, 134.4, 133.5, 132.3, 130.6, 129.7, 129.4, 128.6, 128.4, 128.3, 125.1, 124.0, 123.7, 118.1, 107.1, 55.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{17}O_2$ 337.1229; Found 337.1223.

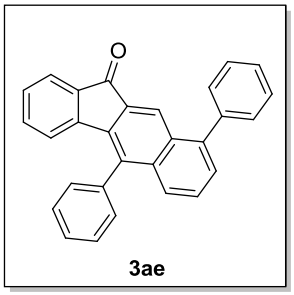
7-isopropyl-5-phenyl-11*H*-benzo[*b*]fluoren-11-one (3ad)



Yellow solid (71.2 mg, 51%). m.p. 166–167 ˚C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.21 (s, 1H), 7.89 (d, J = 8.4 Hz, 1H), 7.7 –7.71 (m, 1H), 7.67–7.57 (m, 3H), 7.45–7.38 (m, 3H), 7.26–7.15 (m, 3H), 6.31 (d, J = 7.3 Hz, 1H), 2.98–2.89 (m, 1H), 1.23 (d, J = 6.9 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.1, 145.2, 137.6, 137.1, 136.6, 135.4, 134.6,

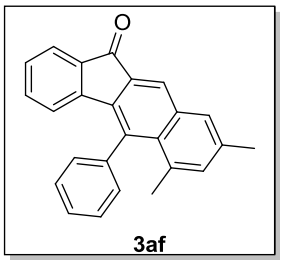
134.4, 131.9, 131.9, 130.8, 129.7, 129.2, 128.5, 128.2, 126.1, 125.0, 124.08, 124.06, 123.7, 34.5, 23.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{21}O$ 349.1592; Found 349.1597.

5,9-diphenyl-11*H*-benzo[*b*]fluoren-11-one (3ae)



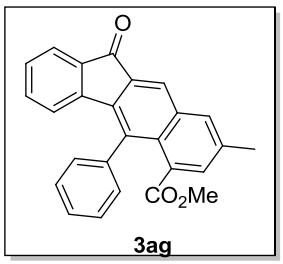
Yellow solid (67.2 mg, 44%). m.p. 208–209 ˚C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.34 (s, 1H), 7.76–7.71 (m, 1H), 7.67–7.61 (m, 3H), 7.58–7.42 (m, 10H), 7.26–7.18 (m, 2H), 6.34 (d, J = 7.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.2, 144.9, 143.4, 134.0, 137.7, 137.3, 136.6, 135.2, 134.8, 134.6, 132.4, 131.7, 130.0, 129.7, 129.3, 128.7, 128.6, 128.3, 128.25, 128.1, 127.7, 126.6, 124.2, 123.8, 123.6. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{18}ONa$ 405.1249; Found 405.1255.

6,8-dimethyl-5-phenyl-11*H*-benzo[*b*]fluoren-11-one (3af)



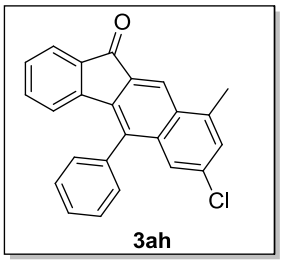
Yellow solid (88.2 mg, 66%). m.p. 193–194 ˚C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11 (d, J = 4.6 Hz, 1H), 7.70 (d, J = 7.3 Hz, 1H), 7.59–7.50 (m, 4H), 7.44–7.39 (m, 2H), 7.17 (td, J_1 = 7.4 Hz, J_2 = 1.6 Hz, 1H), 7.09 (dd, J_1 = 10.6, J_2 = 4.5 Hz, 2H), 5.82 (d, J = 7.8 Hz, 1H), 2.43 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.2, 145.8, 141.5, 136.9, 136.4, 136.4, 136.1, 135.7, 135.4, 135.2, 134.6, 132.8, 131.6, 129.8, 129.7, 128.8, 128.2, 128.1, 125.8, 123.9, 123.86, 25.0, 20.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{19}O$ 335.1436; Found 335.1444.

methyl 9-methyl-11-oxo-5-phenyl-11*H*-benzo[*b*]fluorene-6-carboxylate (3ag)



Yellow solid (81.7 mg, 54%). m.p. 216–217 ˚C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.49 (s, 1H), 7.74 (d, J = 7.3 Hz, 1H), 7.57–7.53 (m, 3H), 7.44–7.38 (m, 3H), 7.35–7.32 (m, 1H), 7.25–7.20 (m, 1H), 7.18–7.11 (m, 1H), 6.00 (d, J = 7.8 Hz, 1H), 3.23 (s, 3H), 2.80 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.1, 170.2, 145.0, 140.1, 137.7, 137.4, 136.5, 134.8, 134.5, 133.5, 132.8, 132.5, 131.9, 131.2, 129.9, 128.9, 128.6, 128.5, 126.9, 124.2, 124.1, 121.6, 51.9, 20.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{19}O_3$ 379.1329; Found 379.1323.

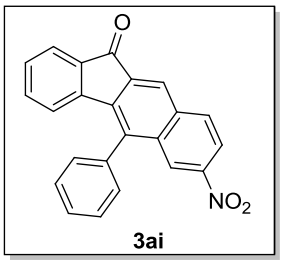
7-chloro-9-methyl-5-phenyl-11*H*-benzo[*b*]fluoren-11-one (3ah)



3ah

Yellow solid (70.9 mg, 50%). m.p. 203–205 ˚C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.39 (s, 1H), 7.74 (d, *J* = 7.1 Hz, 1H), 7.65–7.60 (m, 3H), 7.40–7.36 (m, 2H), 7.29 (d, *J* = 5.1 Hz, 2H), 7.27–7.18 (m, 2H), 6.28 (d, *J* = 7.5 Hz, 1H), 2.75 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.1, 144.7, 139.5, 138.2, 137.0, 136.5, 136.3, 134.8, 134.7, 134.3, 132.3, 131.0, 129.6, 129.4, 128.9, 128.6, 128.4, 124.4, 124.3, 123.9, 121.2, 19.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{16}OCl$ 355.0890; Found 355.0889.

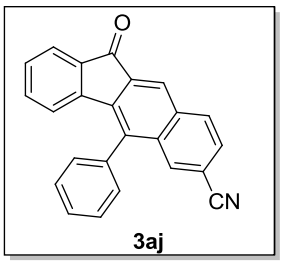
7-nitro-5-phenyl-11*H*-benzo[*b*]fluoren-11-one (3ai)



3ai

Yellow solid (26.3 mg, 25%). m.p. 236–237 ˚C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.36 (d, *J* = 2.0 Hz, 1H), 8.27–8.21 (m, 2H), 8.07 (d, *J* = 11.0 Hz, 1H), 7.76 (d, *J* = 9.0 Hz, 1H), 7.67 (d, *J* = 4.5 Hz, 1H), 7.66–7.65 (m, 3H), 7.43–7.34 (m, 3H), 6.38 (d, *J* = 9.5 Hz, 1H),. ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.2, 147.6, 144.5, 137.2, 136.3, 136.2, 136.1, 135.7, 135.6, 135.3, 132.0, 129.8, 129.7, 129.6, 129.5, 129.2, 124.6, 124.3, 124.2, 123.1, 120.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{14}NO_3$ 352.0974; Found 352.0971.

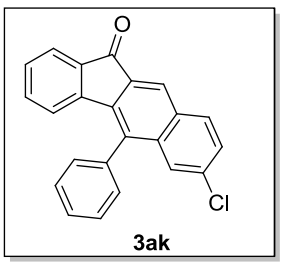
11-oxo-5-phenyl-11*H*-benzo[*b*]fluorene-7-carbonitrile (3aj)



3aj

Yellow solid (16.9 mg, 17%). m.p. 235–236 ˚C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23 (s, 1H), 8.02 (d, *J* = 10.5 Hz, 1H), 7.81 (s, 1H), 7.66 (d, *J* = 4.5 Hz, 1H), 7.65–7.63 (m, 4H), 7.39–7.37 (m, 2H), 7.26–7.23 (m, 2H), 6.37 (d, *J* = 9.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.4, 144.5, 137.0, 136.3, 136.2, 135.9, 135.3, 135.1, 135.0, 134.8, 132.7, 131.6, 129.7, 129.5, 129.1, 127.5, 124.6, 124.5, 124.2, 118.8, 112.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{14}NO$ 332.1075; Found 332.1077.

7-chloro-5-phenyl-11H-benzo[b]fluoren-11-one (3ak)

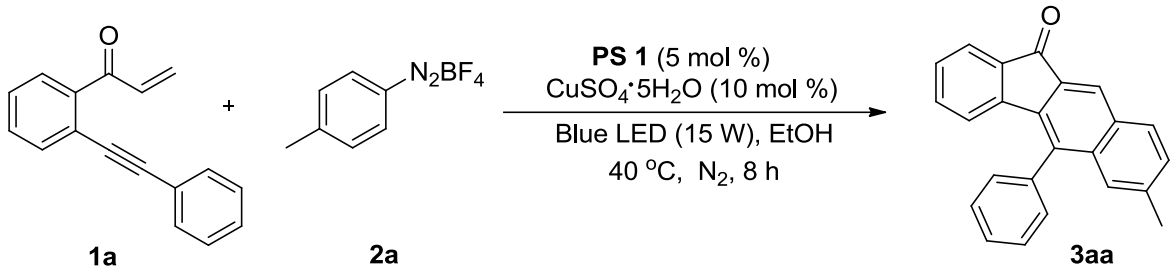


3ak

Yellow solid (30.6 mg, 30%). m.p. 184–185 ˚C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15 (s, 1H), 7.84 (d, *J* = 11.0 Hz, 1H), 7.71 (d, *J* = 9.0 Hz, 1H), 7.62–7.61 (m, 3H), 7.40–7.36 (m, 4H), 7.23–7.18 (m, 2H), 6.30 (d, *J* = 9.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.9, 144.7, 137.8, 136.6, 136.5, 135.3, 134.9, 133.8, 132.8, 132.0, 131.7, 129.6, 129.5, 129.0, 128.7, 127.7, 126.2, 124.8, 124.3, 124.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for

$C_{23}H_{14}ClO$ 341.0733; Found 341.0729.

6. Scale-up experiment

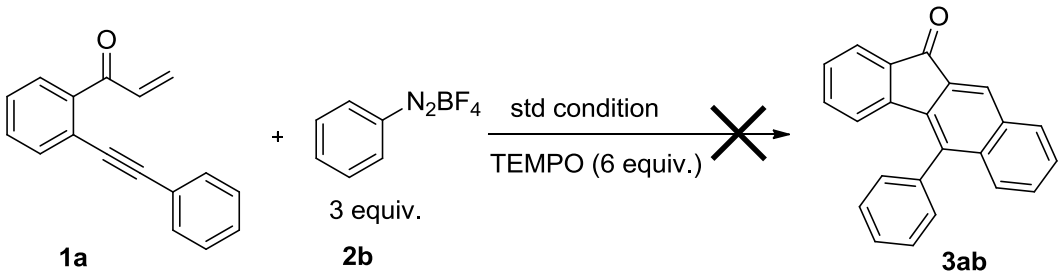


1a (2. 0 mmol, 0.46 g) **2a** (6.0 mmol, 1.23 g) **3aa** (0.32 g, yield: 50%)

4-Methylphenyldiazonium tetrafluorborate **2a** (6.0 mmol, 1.23 g, 3 equiv. based on **1a**), ***PS 1*** (0.12 g, 5 mol % based on **1a**) and $CuSO_4 \cdot 5H_2O$ (50.0 mg, 10 mol % based on **1a**) were placed in a 50 mL Schlenk tube. The tube was evacuated and refilled with N_2 three times. 1-(2-(phenylethynyl)phenyl)prop-2-en-1-one **1a** (0.46 g, 2.0 mmol) and EtOH (20 mL) were added, and the resulting mixture was irradiated with a blue LED lamp (15 W) at 40 ˚C under N_2 atmosphere for 8 h. Upon completion, the reaction mixture was evaporated and purified by column chromatography on silica gel (100-200 mesh), eluting with the indicated mixture of EA/PE (1:20 (v/v)) to give the pure product **3aa** (0.32 g, 50% yield).

7. Mechanistic experiments.

7.1 Radical scavenging experiment

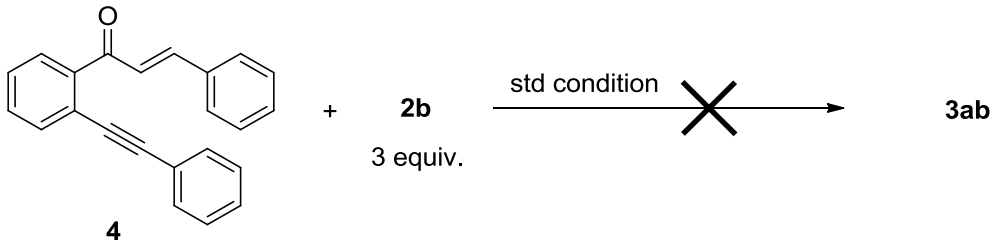


1a **2b** **3ab**

To a 25 mL Schlenk tube were added **1a** (92.9 mg, 0.4 mmol), **2b** (229.2 mg, 1.2 mmol), TEMPO (375.0 mg, 2.4 mmol, 6.0 equiv. based on **1a**), ***PS 1*** (23.0 mg, 5 mol % based on **1a**) and $CuSO_4 \cdot 5H_2O$ (10.0 mg, 10 mol % based on **1a**), the tube was evacuated and refilled with N_2 for three times. Then 4 mL EtOH was added under nitrogen atmosphere. The reaction mixture was irradiated at a distance of 3 cm from 15 W blue LED light. The reaction mixture was stirred at 40 ˚C for 4 h. Upon completion, the reaction mixture was sent for GC analysis

and none of the desired product **3ab** was detected.

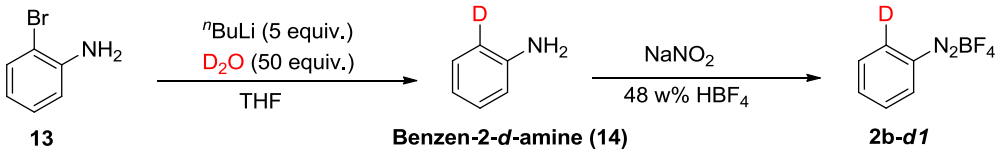
7.2 Subjection of 4 to the standard reaction conditions.



To a 25 mL Schlenk tube were added **4**[6] (123.2 mg, 0.4 mmol), **2b** (229.2 mg, 1.2 mmol), ***PS 1*** (23.0 mg, 5 mol % based on **4**) and $CuSO_4 \cdot 5H_2O$ (10.0 mg, 10 mol % based on **4**), the tube was evacuated and refilled with N_2 for three times. Then 4 mL EtOH was added under nitrogen atmosphere. The reaction mixture was irradiated at a distance of 3 cm from 15 W blue LED light. The reaction mixture was stirred at 40 ˚C for 4 h. Upon completion, the reaction mixture was sent for GC analysis and none of the desired product **3ab** was detected. The starting material **4** was almost quantitatively recovered.

7.3 Intramolecular H/D competition experiment

Synthesis of 2b-*d*$_1$[7]

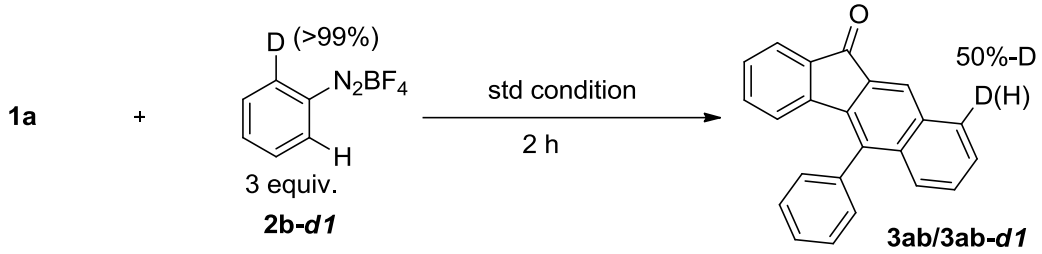


In a 100 mL of flask, ^{n}BuLi (80 mmol, 32 mL, 2.5 M in hexane) was added to 2-bromoaniline **13** (16 mmol, 2.75 g) in THF (20 mL) under N_2 atmosphere, and the mixture was stirred at -78 ˚C for 1 h. Then the mixture was warmed to rt and stirred for 1 h. D_2O (0.8 mol, 14.4 mL) was added to the reaction at -78 ˚C, which was warmed to rt and stirred for 1 h. The reaction mixture was quenched with water (20 mL) and extracted with ethyl acetate (50 mL×2). The organic layer were combined, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by chromatography to give **Benzen-2-*d*-amine 14** (601 mg, 40%) whose deuterated rate is >99%.

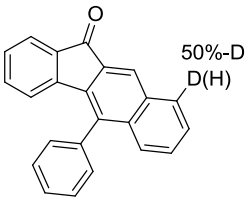
Benzen-2-*d*-amine 14 (5 mmol, 470 mg) was added to a mixture of 50% HBF_4 (1.5 mL) and distilled water (3 mL) in ice bath. To this solution, an ice-cold solution of sodium nitrite (352 mg, 1.02 equiv.) in distilled water (1.5 mL) was added. After stirring for 30 mins, the

precipitate was collected on a hirch funnel and washed with small amount of ice-cold distilled water. The solid was dissolved in acetone and precipitated with slow addition of ethyl ether. **2b-*d1*** were obtained after repeat this trituration two to three times. (771 mg, 80%).

Subjection 2b-*d1* to react with 1a under the standard reaction conditions:

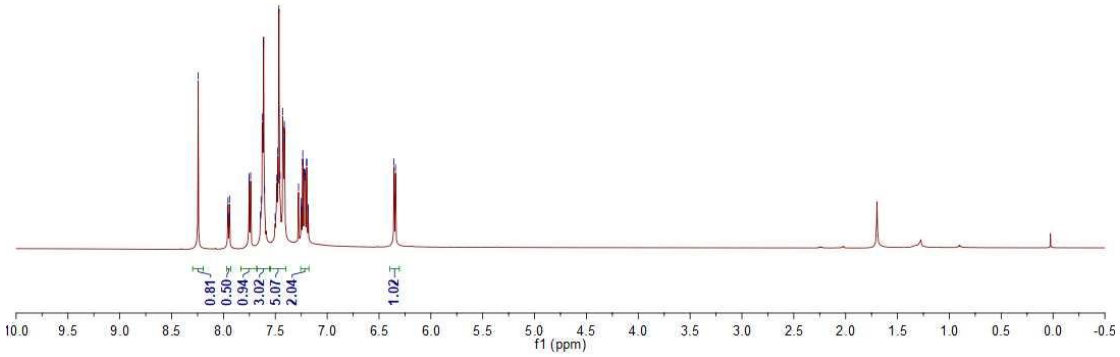


1a (92.9 mg, 0.4 mmol), **2b-*d1*** (231.5 mg, 1.2 mmol), ***PS 1*** (23.0 mg, 5 mol % based on **1a**) and $CuSO_4 \cdot 5H_2O$ (10.0 mg, 10 mol % based on **1a**), the tube was evacuated and refilled with N_2 for three times. Then 4 mL EtOH was added under nitrogen atmosphere. The reaction mixture was irradiated at a distance of 3 cm from 15 W blue LED light. The reaction mixture was stirred at 40 ˚C for 2 h. Upon completion, the reaction mixture was evaporated and purified by column chromatography on silica gel (100-200 mesh), eluting with the indicated mixture of EA/PE (1:20 (v/v)) to give the pure product **3ab**/**3ab-*d1*** (46.9 mg, 40%)**.** The ^{1}H NMR spectra of **3ab**/**3ab-*d*1** and the calculated D incorporated rate are listed as below:



3ab/3ab-*d1*

k_H / k_D = 1.0



Analytical data of **3ab**/**3ab-*d1***: ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.24 (s, 1H), 7.94 (d, J = 7.3 Hz, 0.5H), 7.74 (d, J = 7.0 Hz, 1H), 7.65–7.59 (m, 3H), 7.50–7.40 (m, 5H), 7.25–7.17 (m, 2H), 6.35 (d, J = 7.4 Hz, 1H).

When **2b-*d1*** was used, the reaction did not exhibit a primary kinetic isotope effect in the intramolecular competition experiment (k_H/k_D = 1.0), suggesting that the C-H bond cleavage in the late-stage cyclization process is not the rate-determining step.

8. References

[1] J. Zhang, Y. Xiao, K. Chen, W. Wu, H. Jiang and S. Zhu, *Adv. Synth. Catal.*, 2016, **358**, 2684.

[2] A. Ahrens, N. Heinrich, F. Niklas, S. R. Kohl, M. Hokamp, M. Rodolph, F. Rominger and A. S. K. Hashmi, *Adv. Synth. Catal.*, 2019, **361**, 5605.

[3] P. Hanson, J. R. Jones, A. B. Taylor, P. H. Walton and A. W. Timms, *J. Chem. Soc., Perkin Trans. 2*, 2002, 1135.

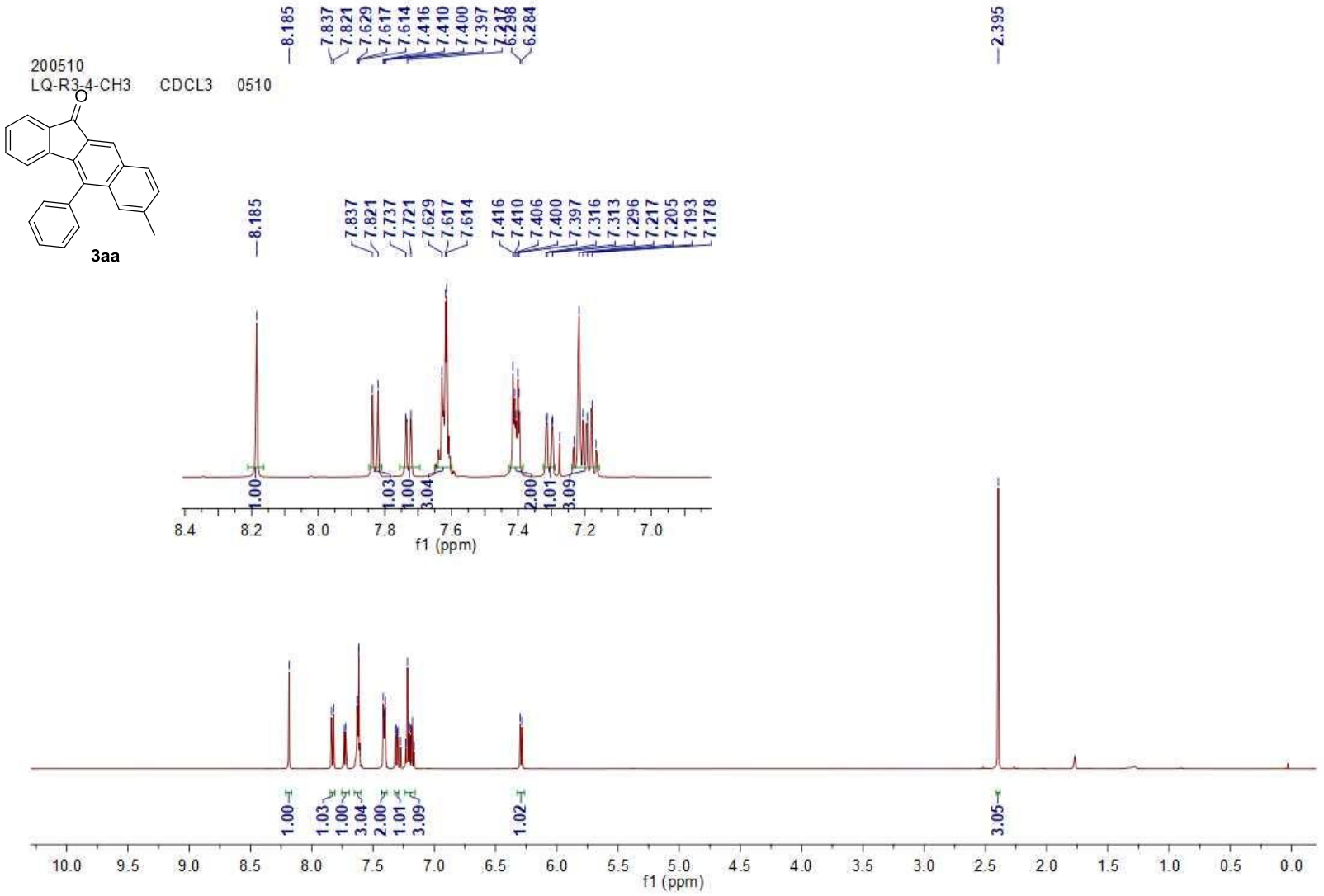
[4] L. Zheng, H. Xue, B. Zhou, S.-P. Luo, H. Jin and Y. Liu, *Org. Lett.*, 2021, **23**, 4478.

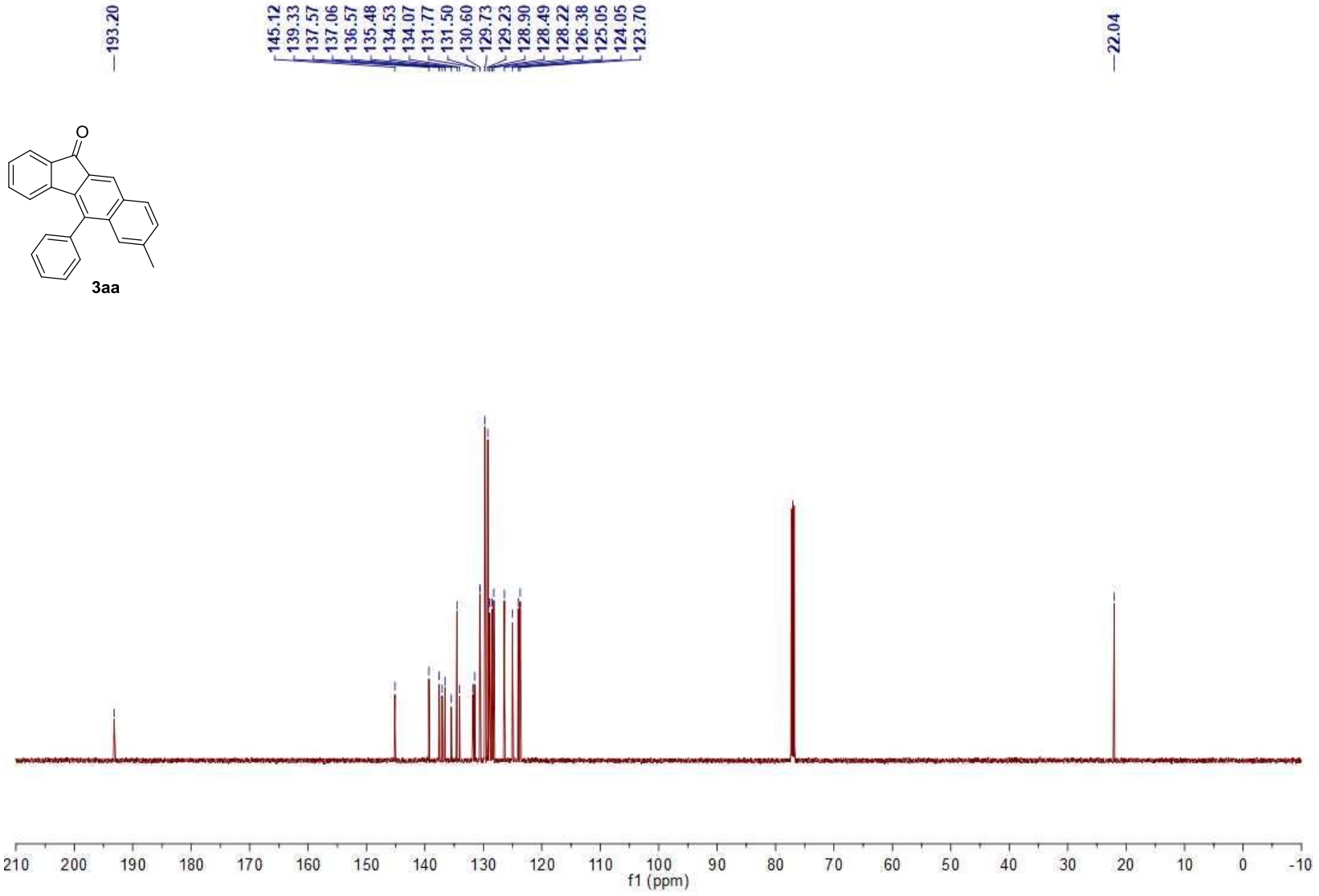
[5] W. Ried and G. Clauss, *Justus Liebigs Ann. Chem.* 1975, 953.

[6] L. Zheng, B. Zhou, H. Jin, T. Li and Y. Liu, *Org. Lett.*, 2018, **20**, 7053.

[7]. Y.-X.Wang, F.-P. Zhang, Y.-X. Luan and M. Ye, *Org. Lett.*, 2020, **22**, 2230-2234

9. ^{1}H and ^{13}C NMR spectra of unknown starting materials.

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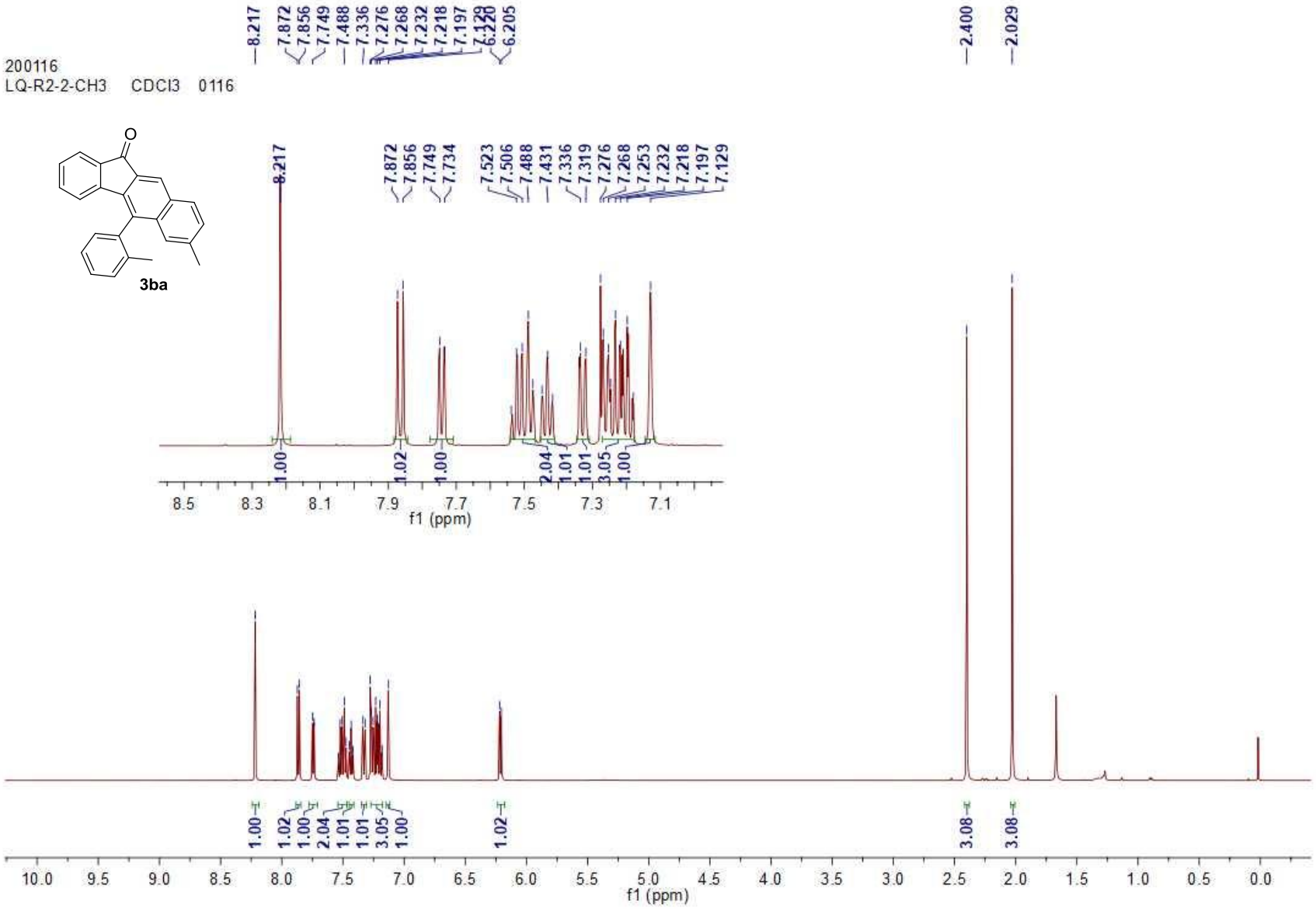
145.12
139.33
137.57
137.06
136.57
135.48
134.53
134.07
131.77
131.50
130.60
129.73
129.23
128.90
128.49
128.22
126.38
125.05
124.05
123.70
22.04
O
3aa
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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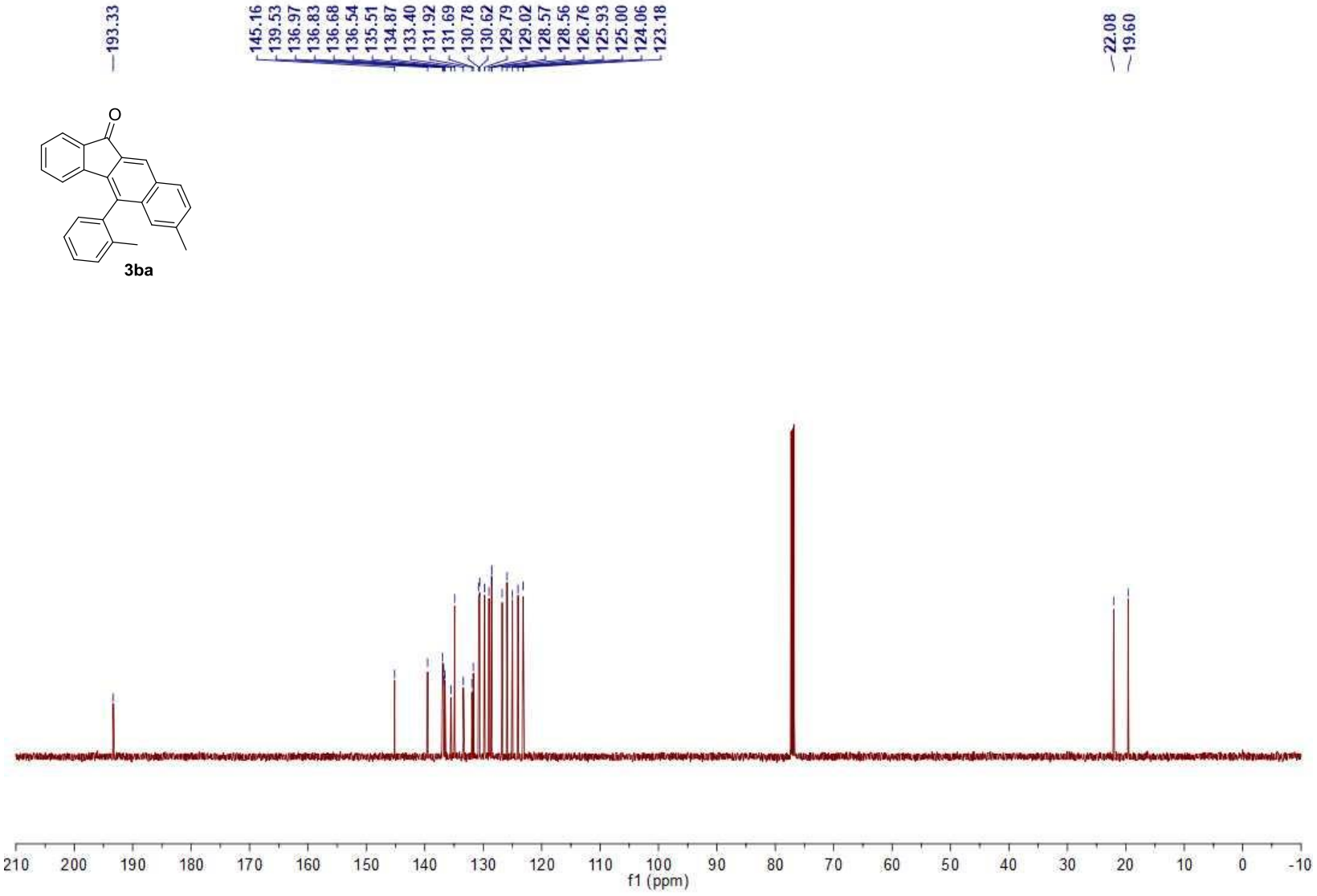
LQ-R2-2-CH3 CDCl3 0116
3ba
f1 (ppm)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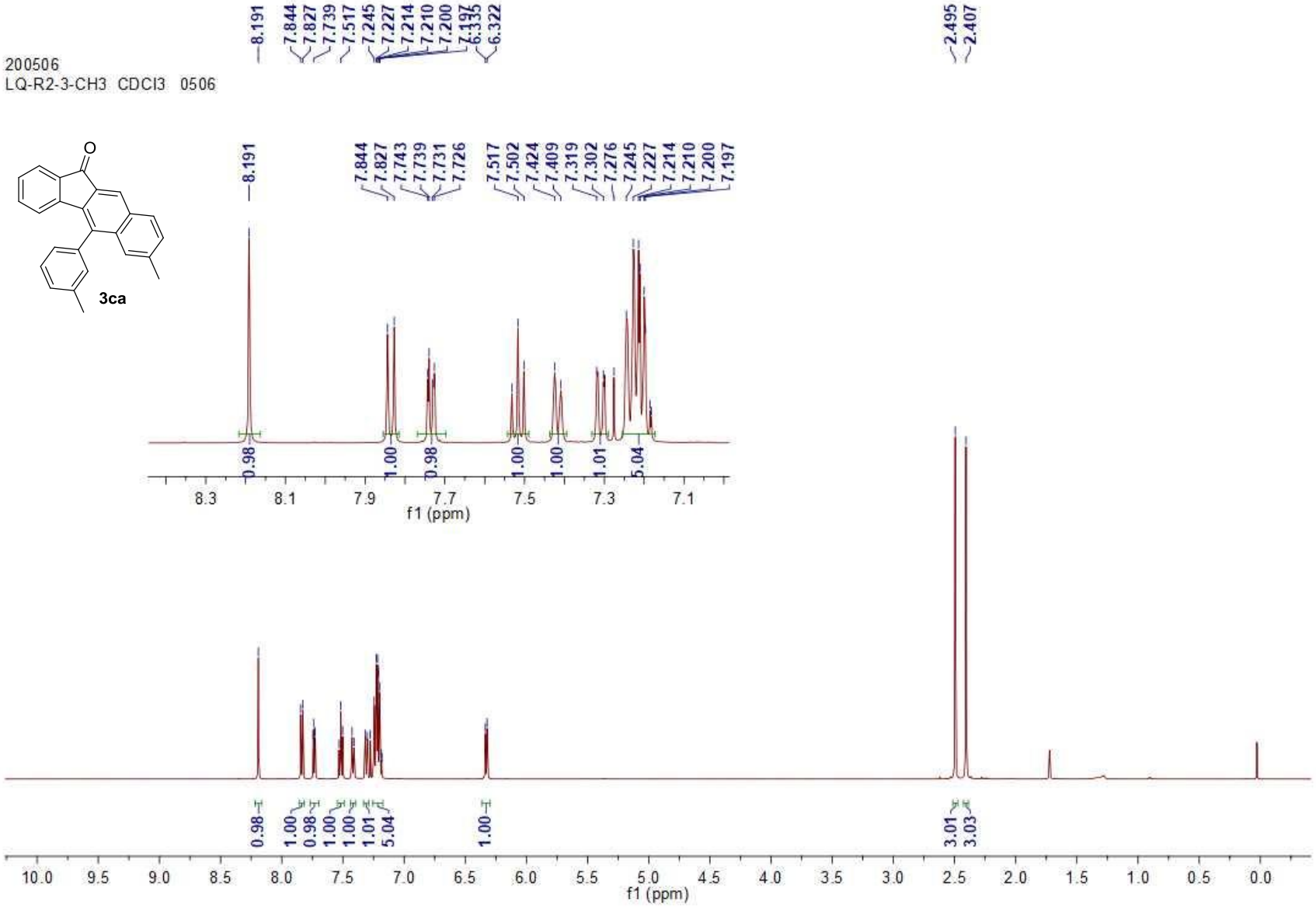
145.16
139.53
136.97
136.83
136.68
136.54
135.51
134.87
133.40
131.92
131.69
130.78
130.62
129.79
129.02
128.57
128.56
126.76
125.93
125.00
124.06
123.18
22.08
19.60
O
3ba
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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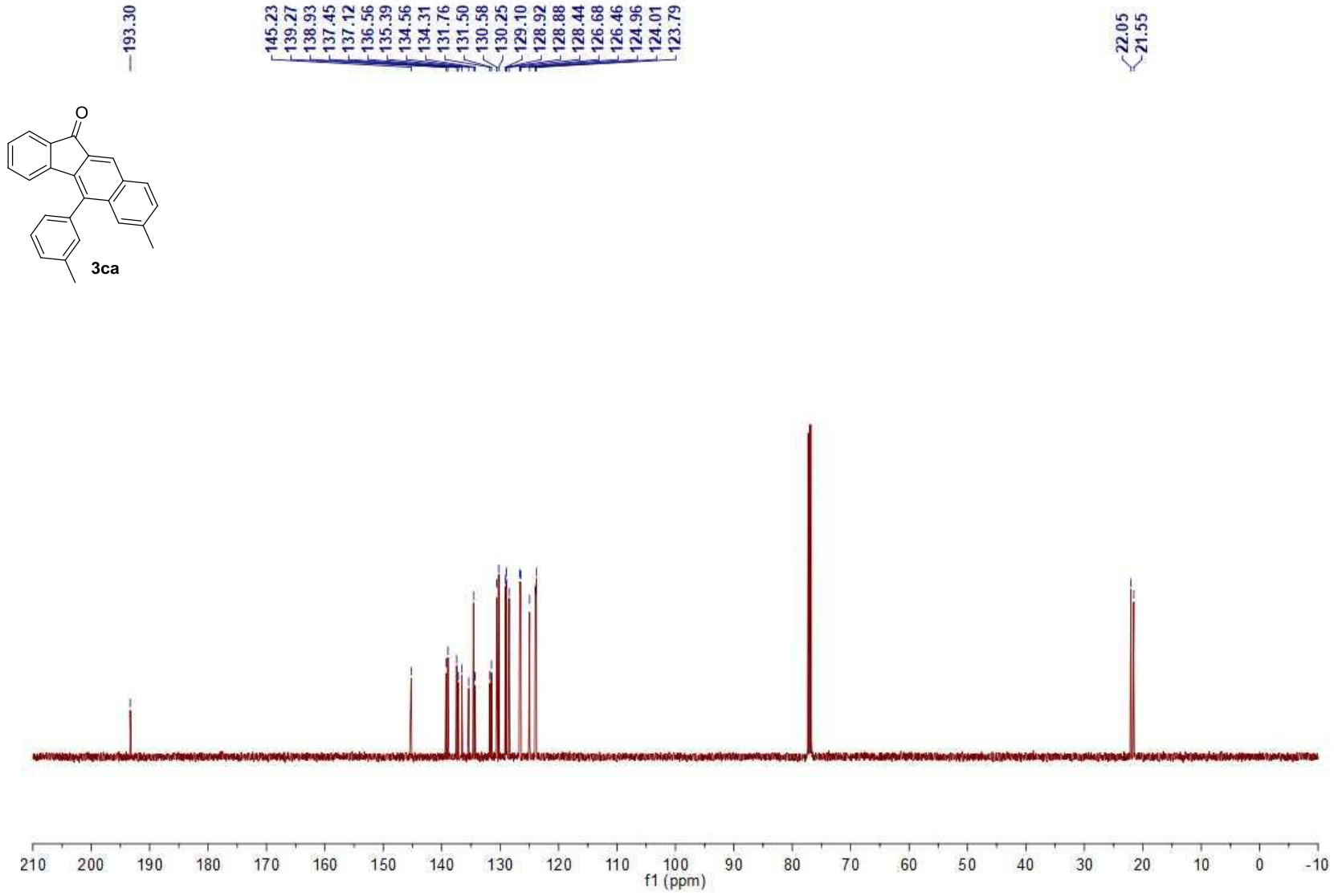
7.827
7.739
7.517
7.245
7.227
7.214
7.210
7.200
7.197
6.335
6.322
2.495
2.407
O
3ca
7.844
7.827
7.743
7.739
7.731
7.726
7.517
7.502
7.424
7.409
7.319
7.302
7.276
7.245
7.227
7.214
7.210
7.200
7.197
0.98
1.00
0.98
1.00
1.00
1.01
5.04
8.3
8.1
7.9
7.7
7.5
7.3
7.1
f1 (ppm)
0.98
1.00
0.98
1.00
1.00
1.01
5.04
1.00
3.01
3.03
10.0
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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137.12
136.56
135.39
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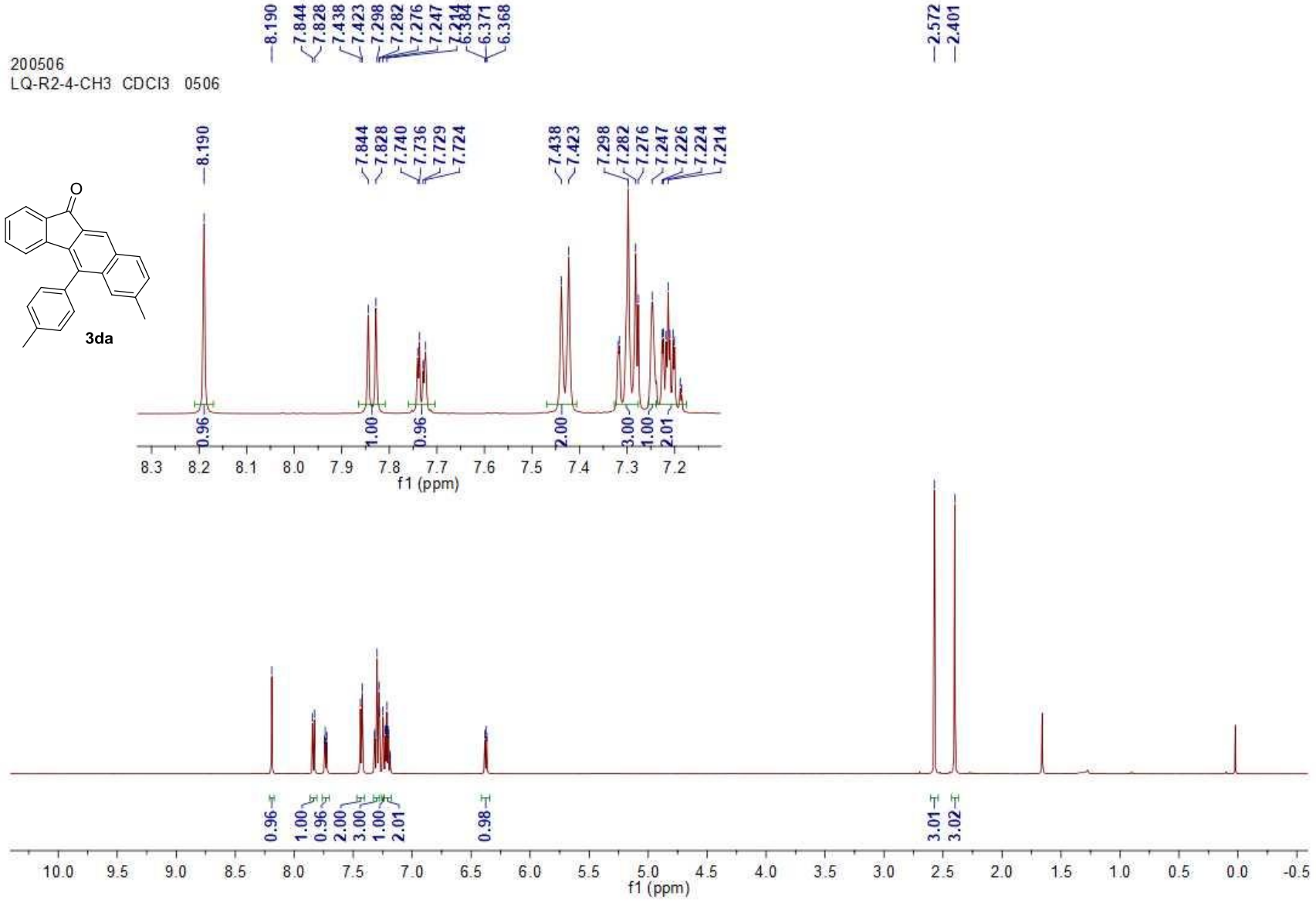
131.76
131.50
130.58
130.25
129.10
128.92
128.88
128.44
126.68
126.46
124.96
124.01
123.79
22.05
21.55
O
3ca
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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LQ-R2-4-CH3 CDCl3 0506
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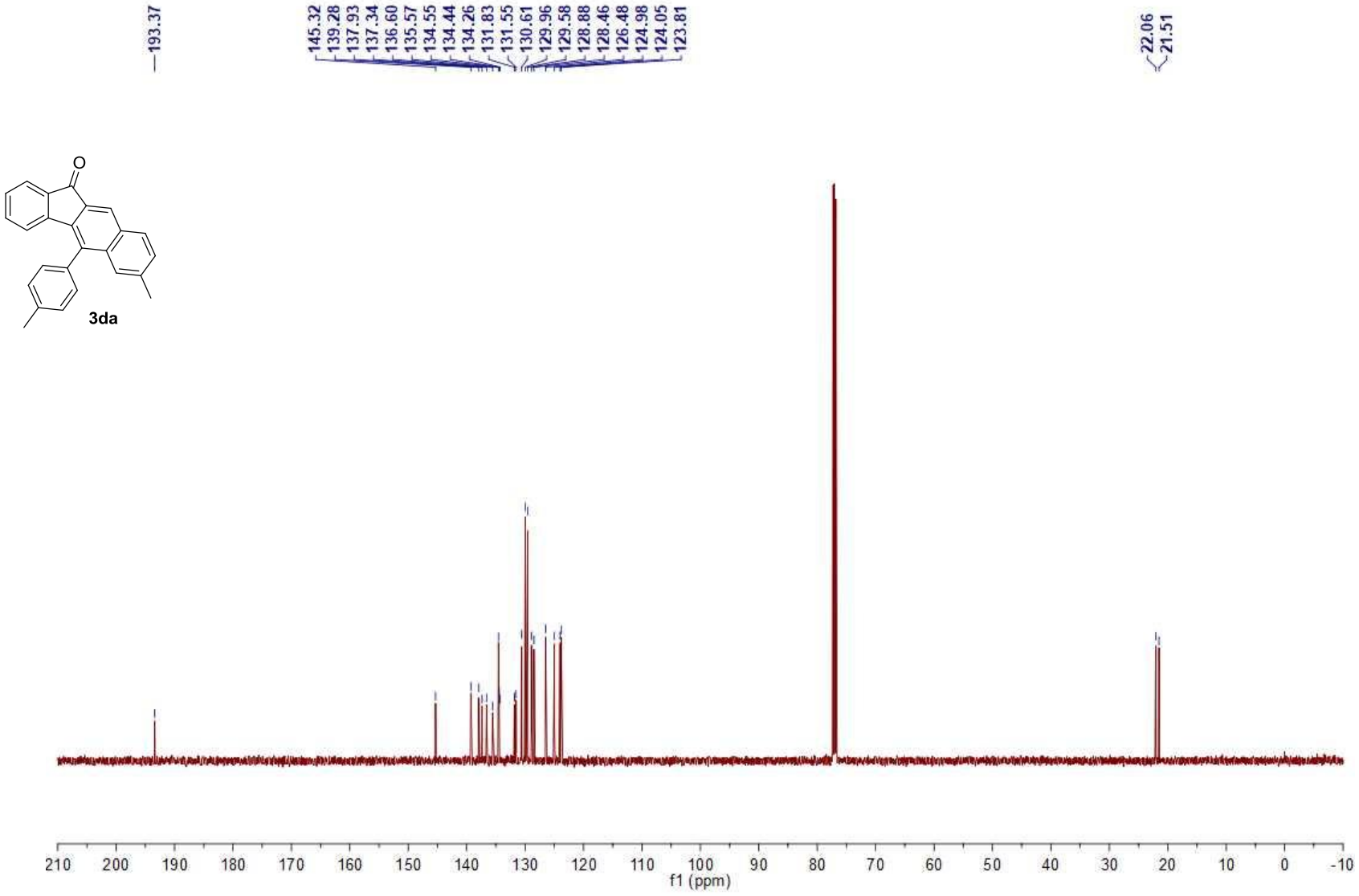
7.276
7.247
7.371
6.368
2.572
2.401
7.740
7.736
7.729
7.724
7.226
7.224
7.214
O
3da
0.96
1.00
0.96
2.00
3.00
1.00
2.01
0.98
3.01
3.02
f1 (ppm)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137.34
136.60
135.57
134.55
134.44
134.26
131.83
131.55
130.61
129.96
129.58
128.88
128.46
126.48
124.98
124.05
123.81
22.06
21.51
O
3da
210
200
190
180
170
160
150
140
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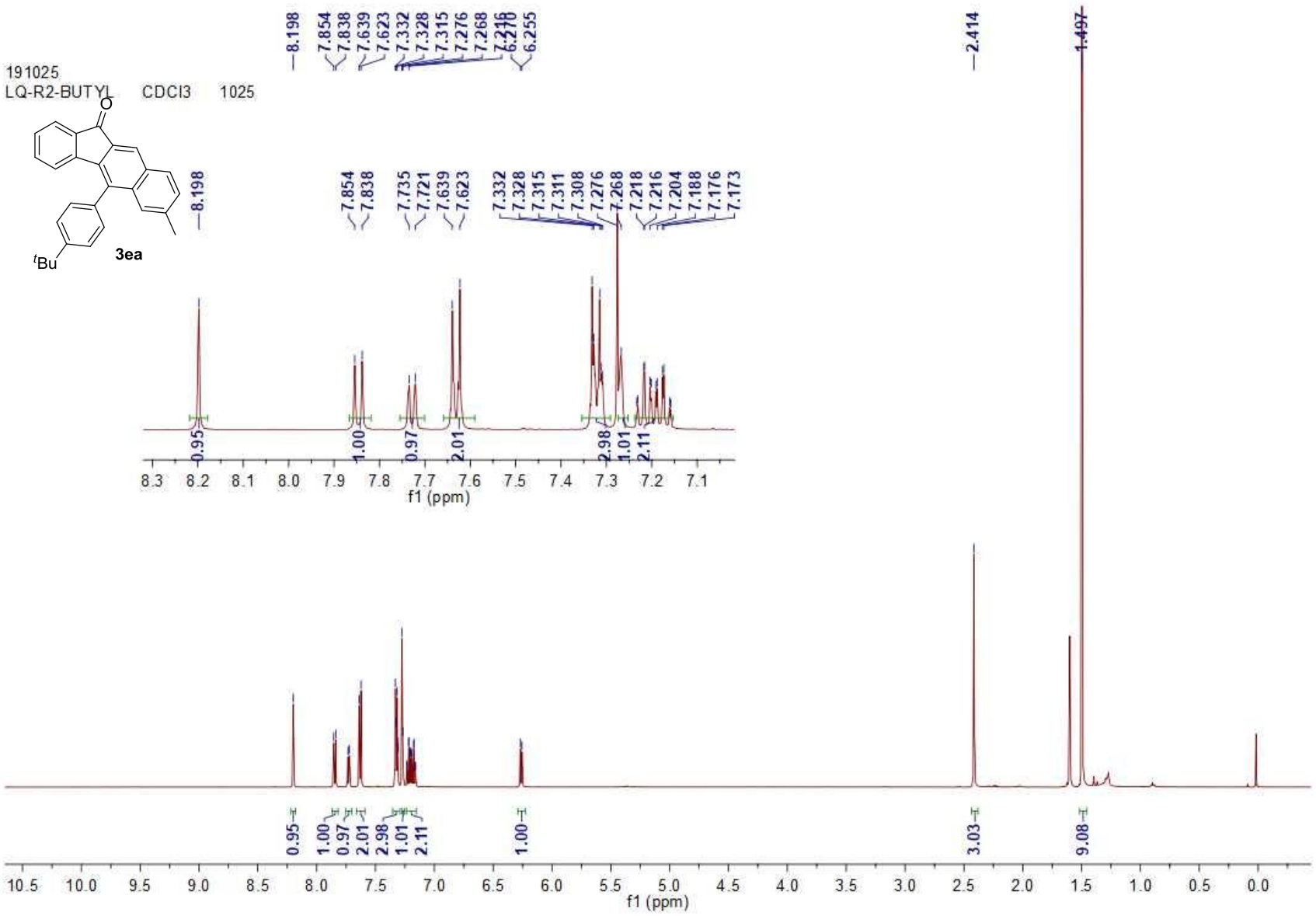
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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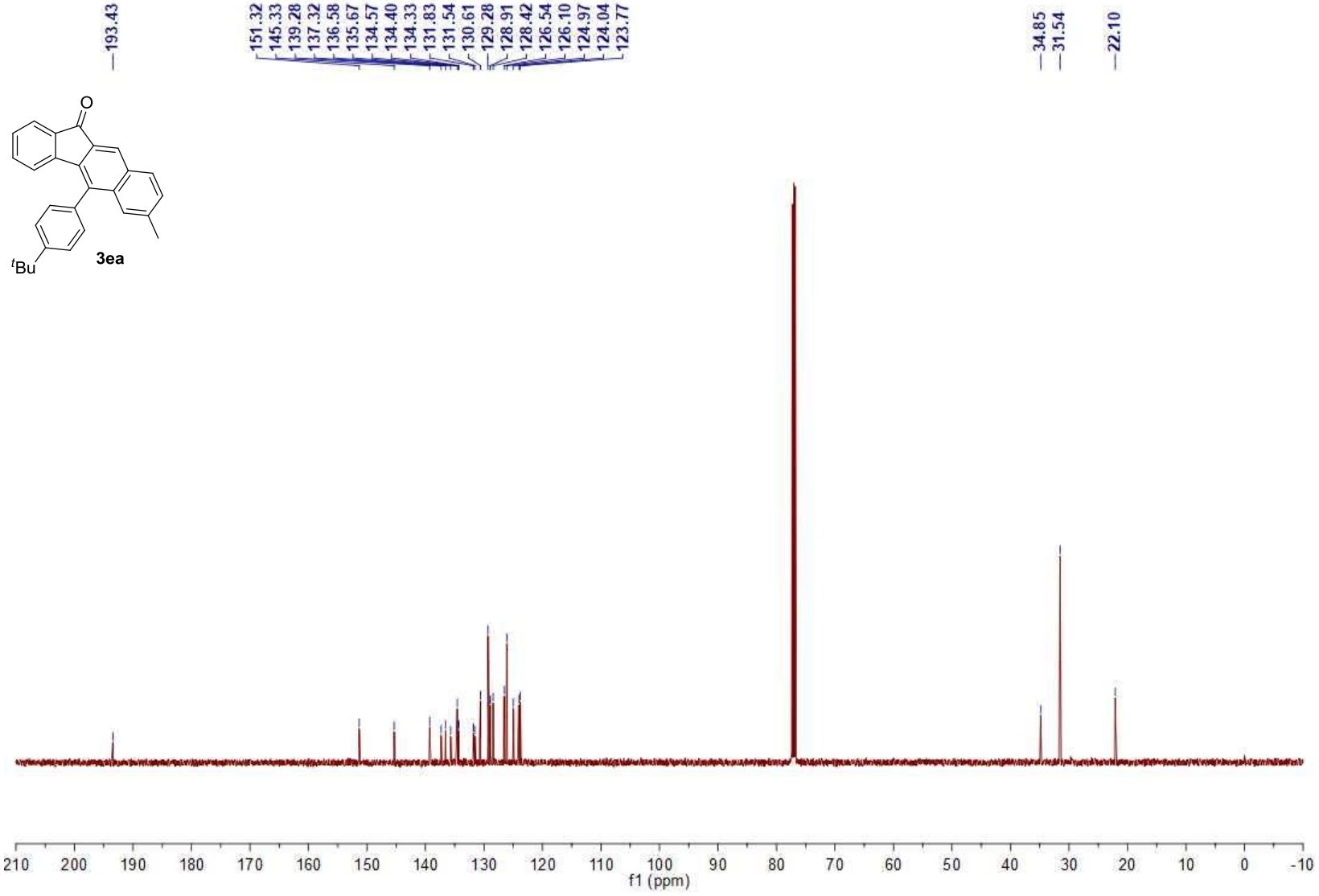
LQ-R2-BUTYL CDCl3 1025
3ea
f1 (ppm)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134.57
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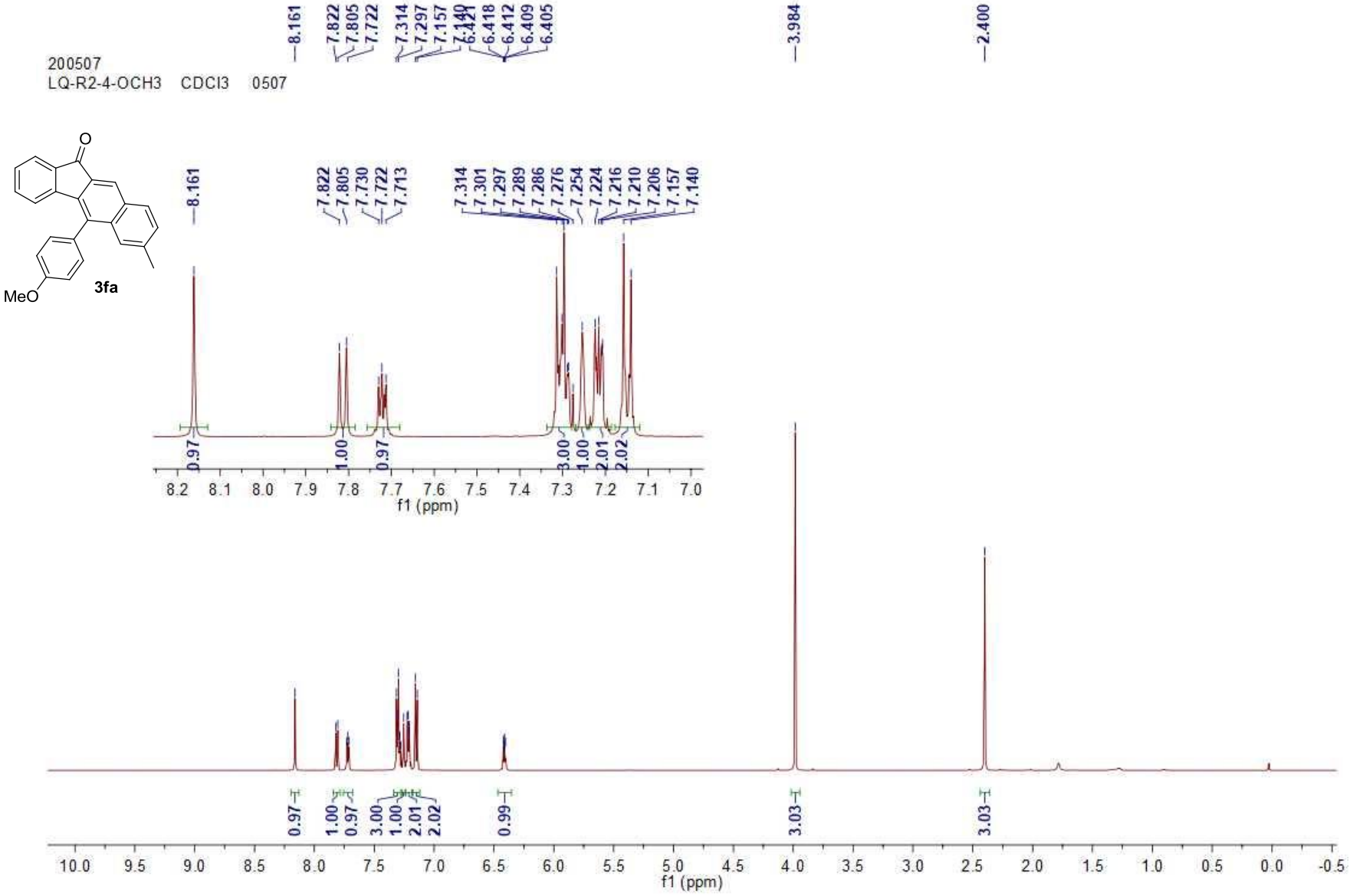
134.33
131.83
131.54
130.61
129.28
128.91
128.42
126.54
126.10
124.97
124.04
123.77
34.85
31.54
22.10
O
tBu
3ea
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.722
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6.412
6.409
6.405
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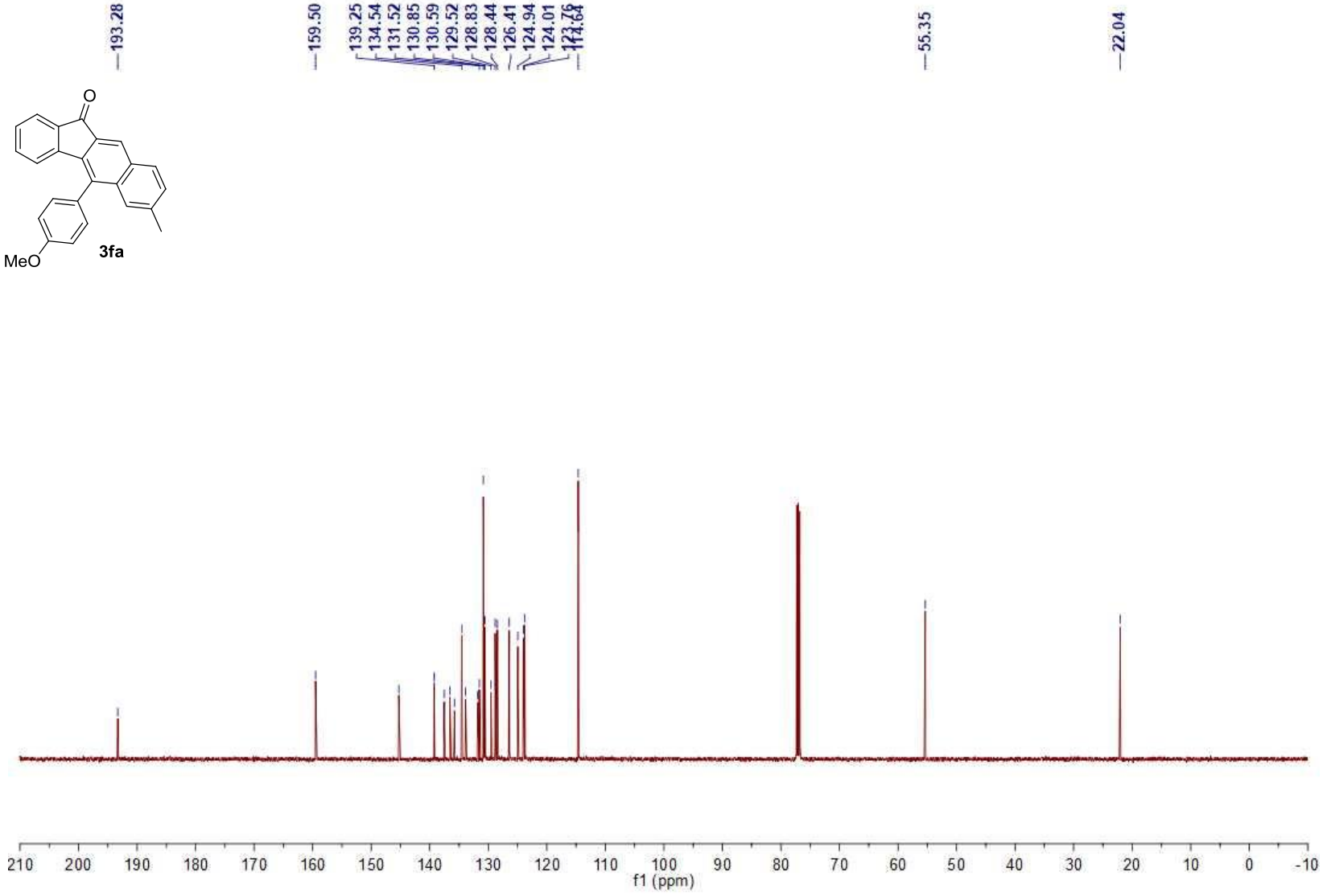
2.400
O
MeO
3fa
f1 (ppm)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131.52
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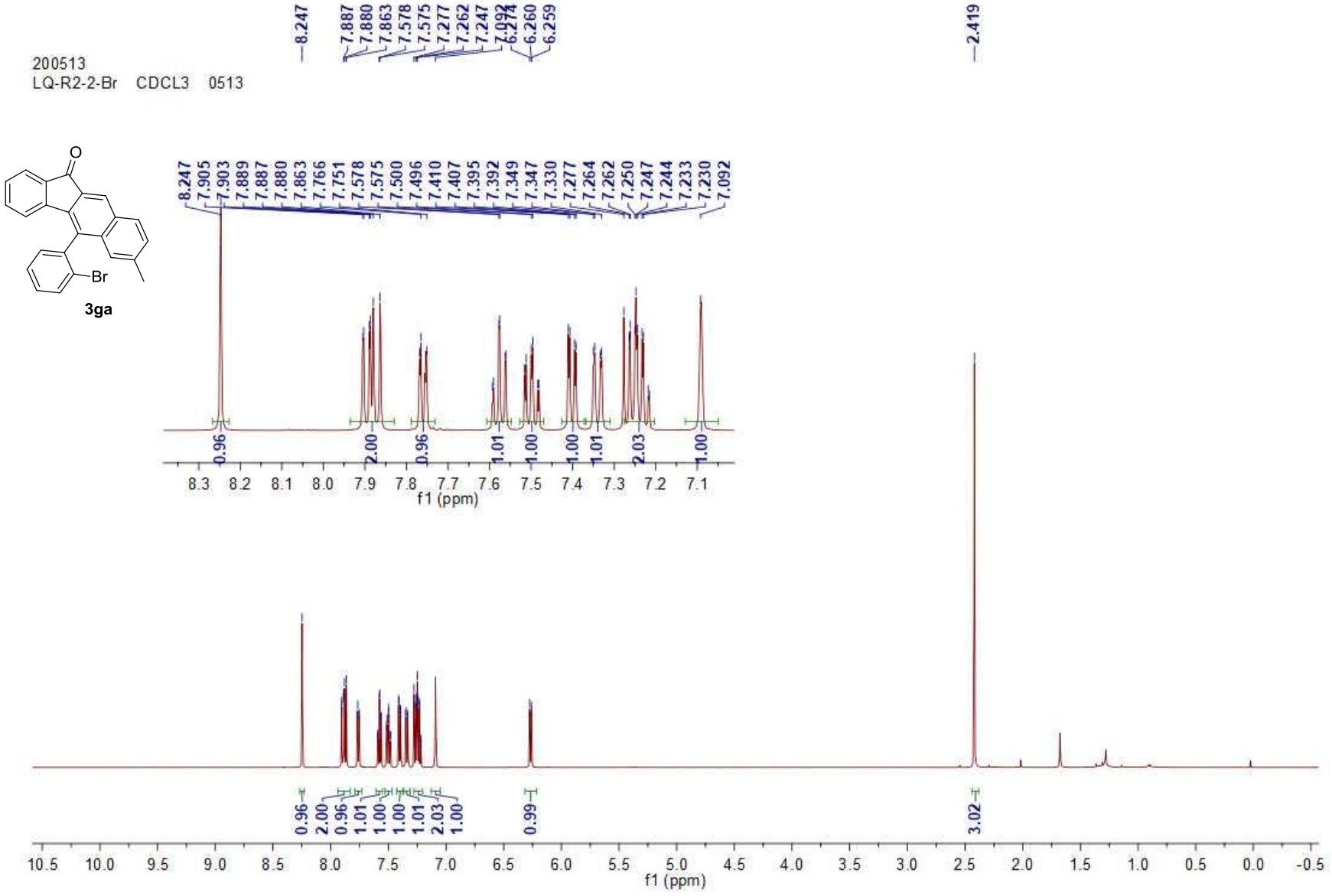
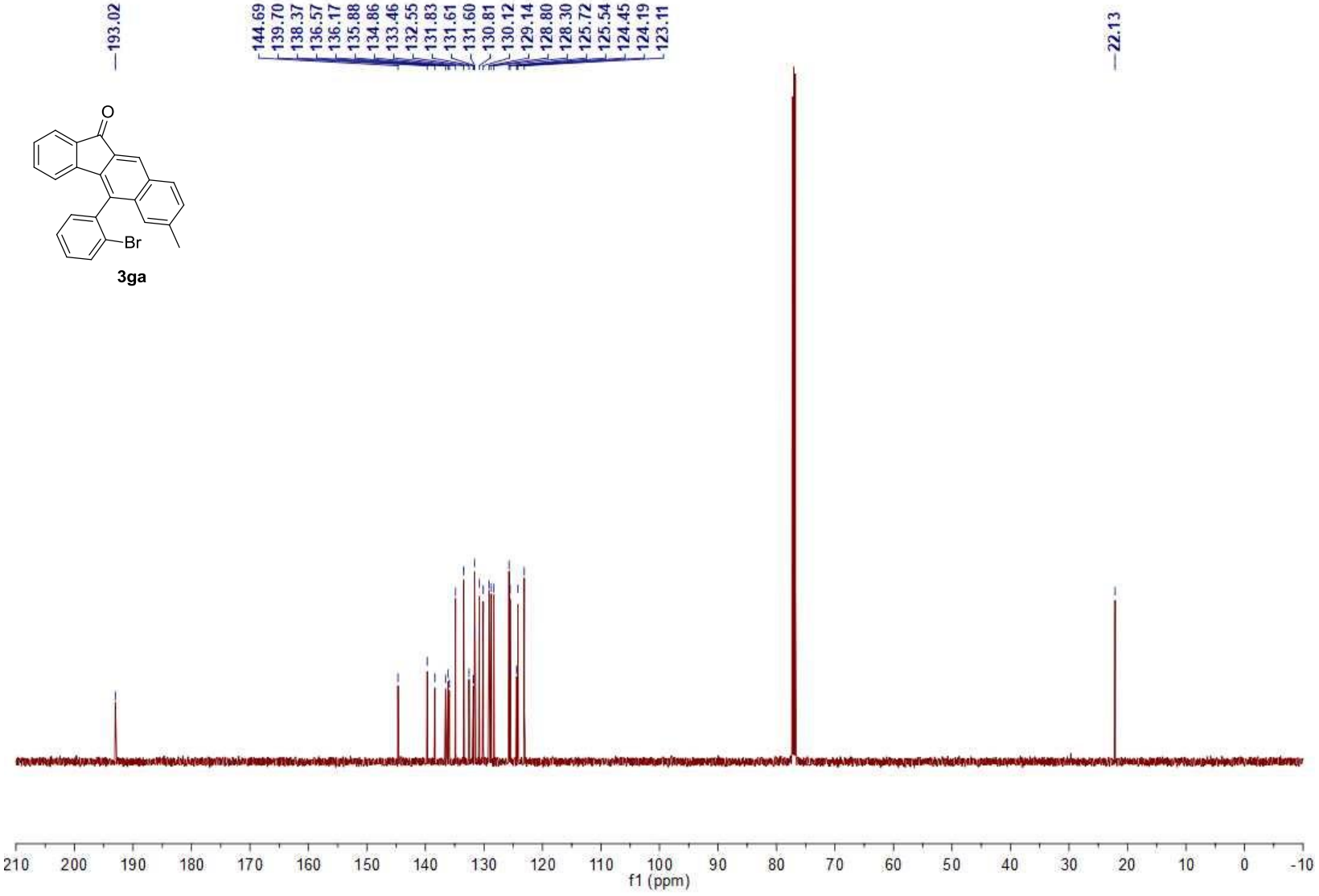
124.01
55.35
22.04
O
MeO
3fa
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


200513
LQ-R2-2-Br CDCL3 0513
3ga
f1 (ppm)
f1 (ppm)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130.81
130.12
129.14
128.80
128.30
125.72
125.54
124.45
124.19
123.11
22.13
O
Br
3ga
210
200
190
180
170
160
150
140
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120
110
100
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80
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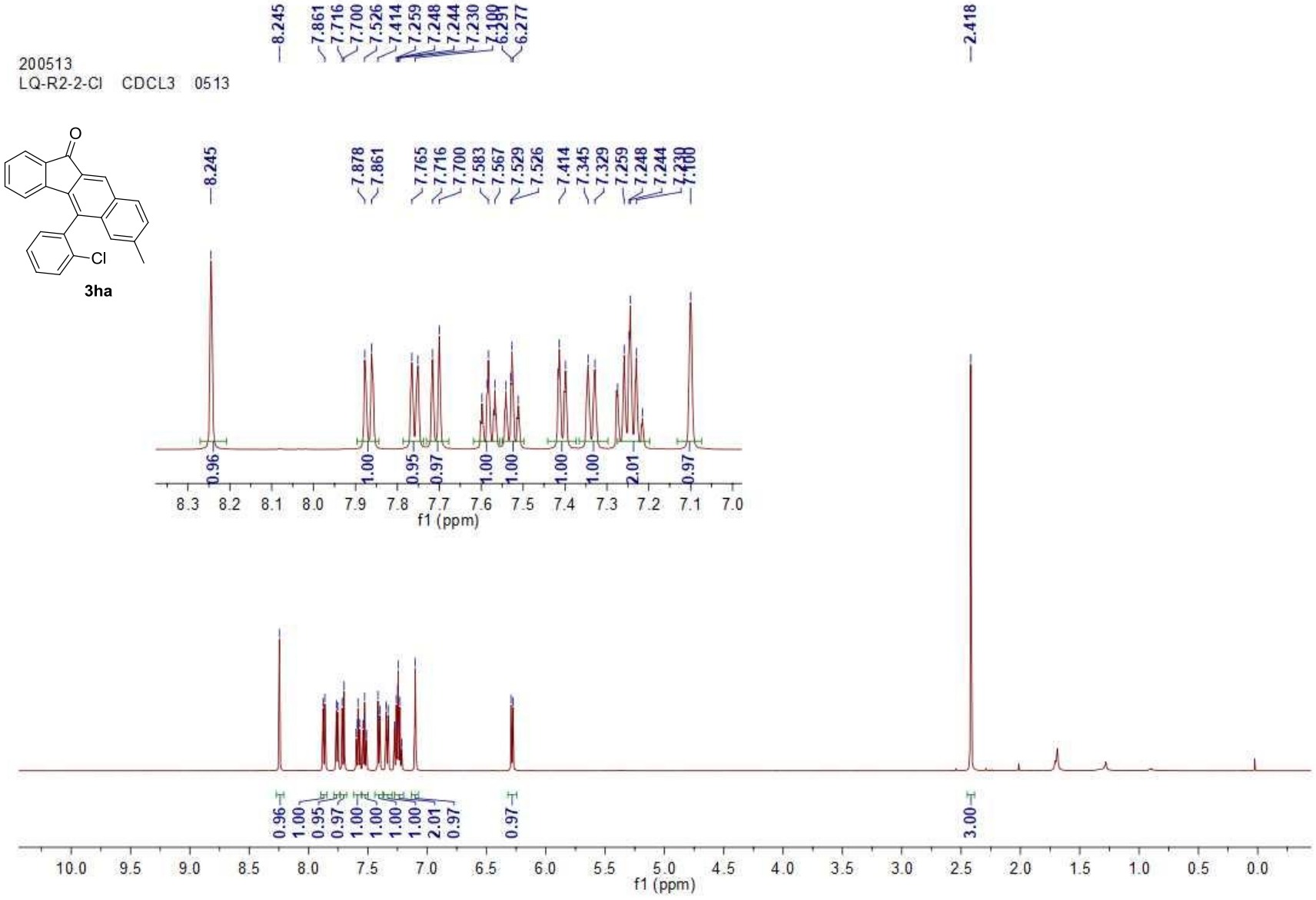
40
30
20
10
0
-10
f1 (ppm)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7.244
7.230
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7.878
7.765
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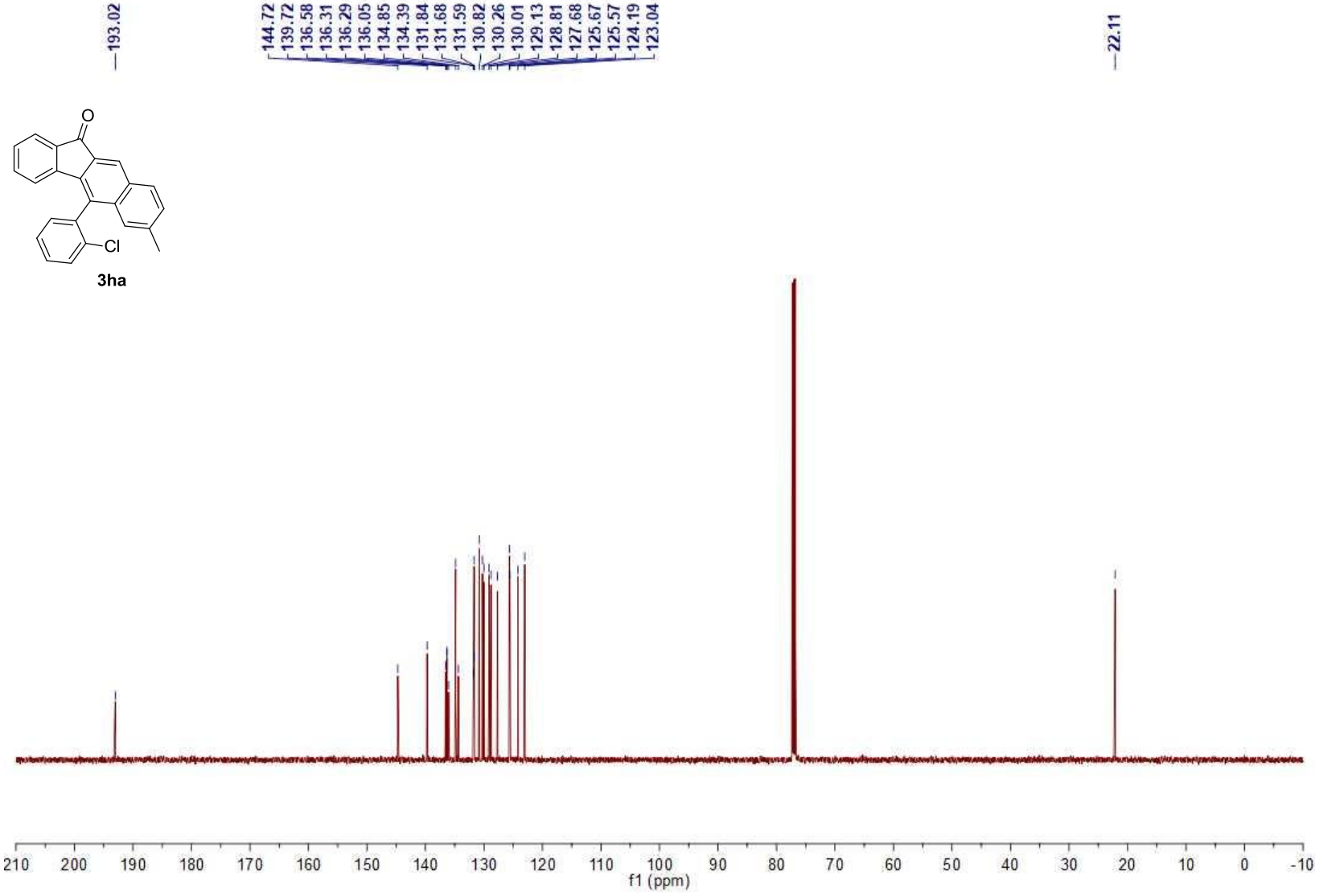
3.00
f1 (ppm)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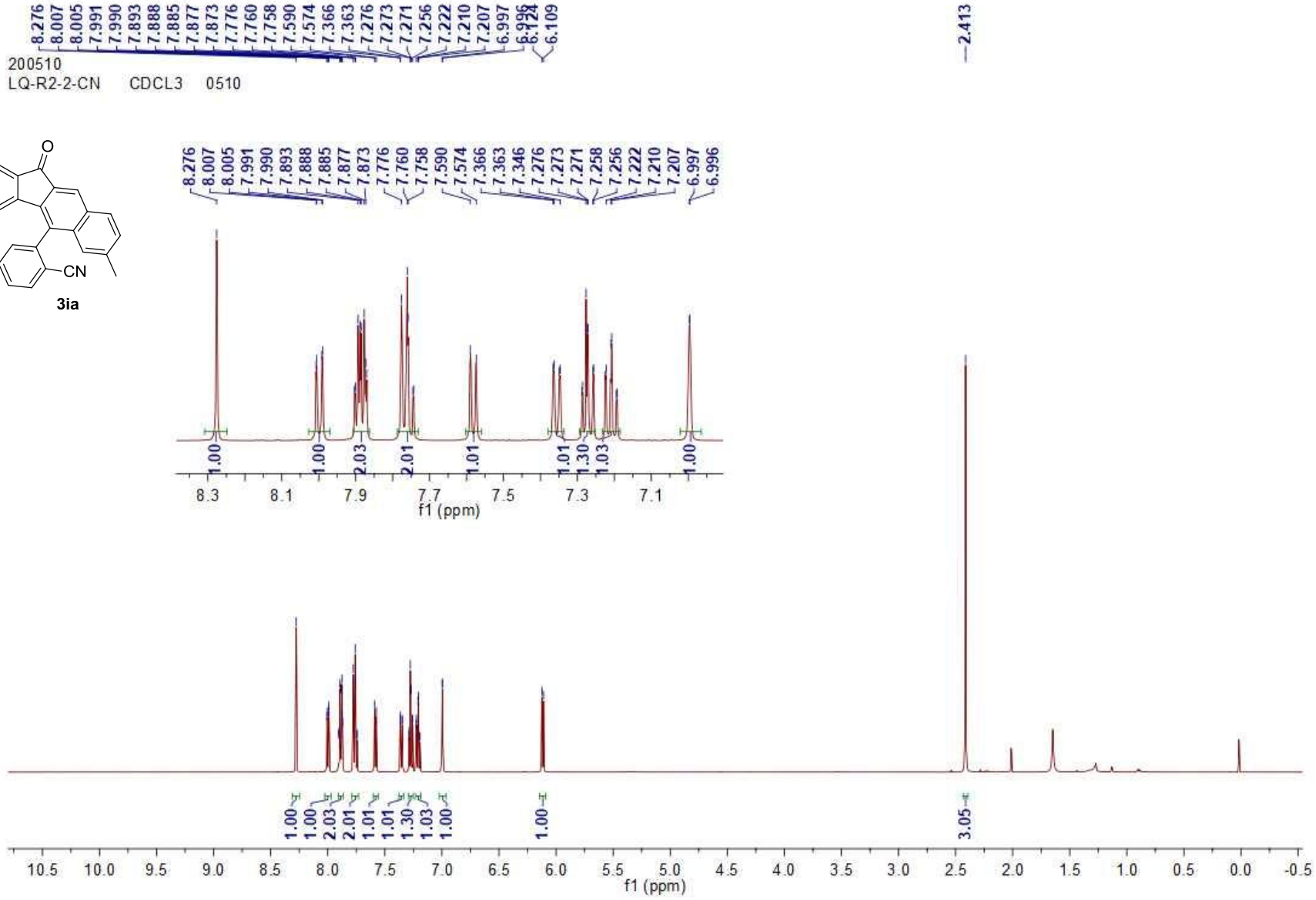
131.84
131.68
131.59
130.82
130.26
130.01
129.13
128.81
127.68
125.67
125.57
124.19
123.04
22.11
O
Cl
3ha
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.885
7.877
7.873
7.776
7.760
7.758
7.590
7.574
7.366
7.363
7.276
7.273
7.271
7.256
7.222
7.210
7.207
6.997
6.996
6.124
6.109
200510
LQ-R2-2-CN CDCL3 0510
2.413
O
CN
3ia
8.276
8.007
8.005
7.991
7.990
7.893
7.888
7.885
7.877
7.873
7.776
7.760
7.758
7.590
7.574
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7.363
7.346
7.276
7.273
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7.258
7.256
7.222
7.210
7.207
6.997
6.996
1.00
1.00
2.03
2.01
1.01
1.01
1.30
1.03
1.00
8.3
8.1
7.9
7.7
7.5
7.3
7.1
f1 (ppm)
1.00
1.00
2.03
2.01
1.01
1.01
1.30
1.03
1.00
1.00
3.05
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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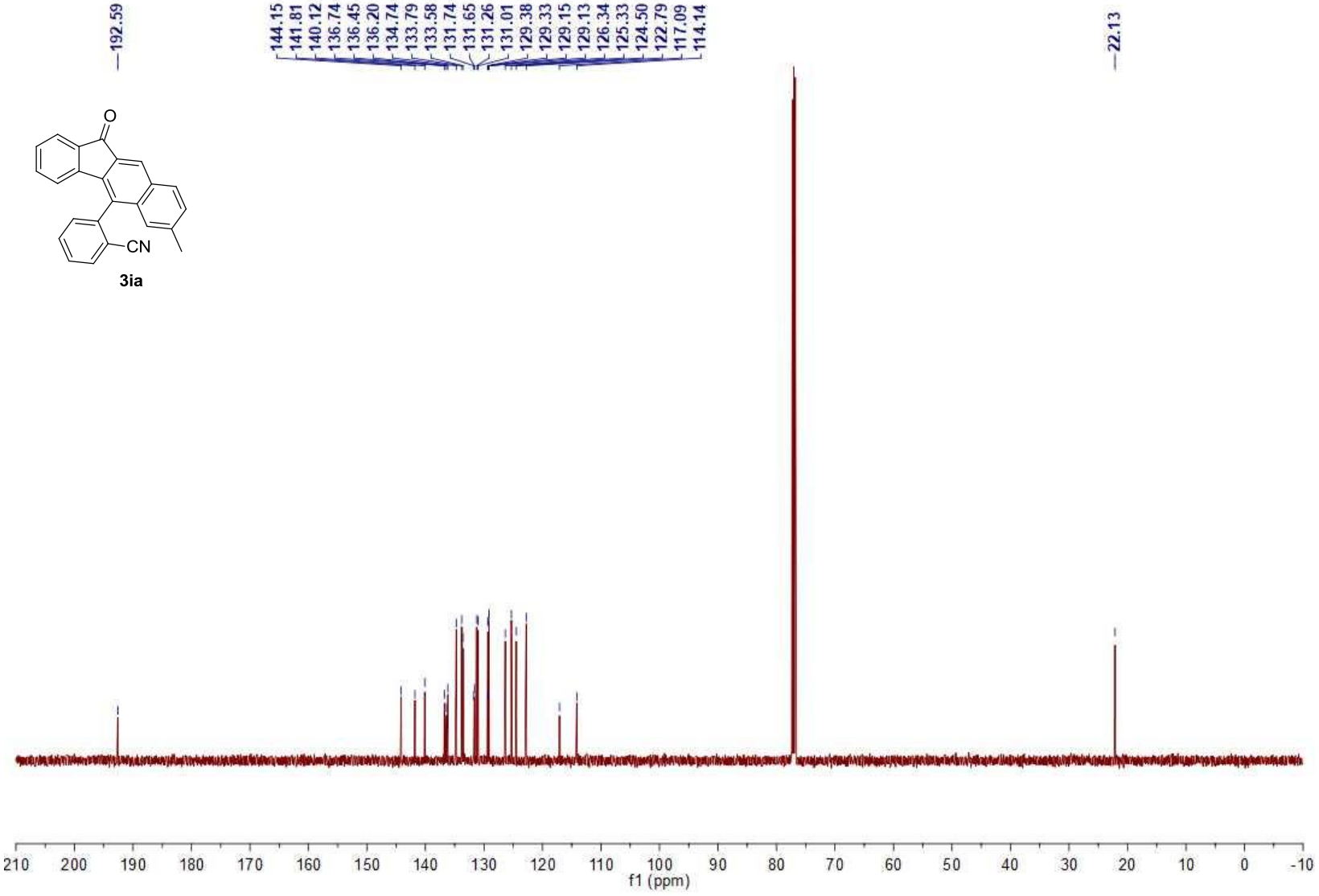
f1 (ppm)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131.26
131.01
129.38
129.33
129.15
129.13
126.34
125.33
124.50
122.79
117.09
114.14
22.13
O
CN
3ia
210
200
190
180
170
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30
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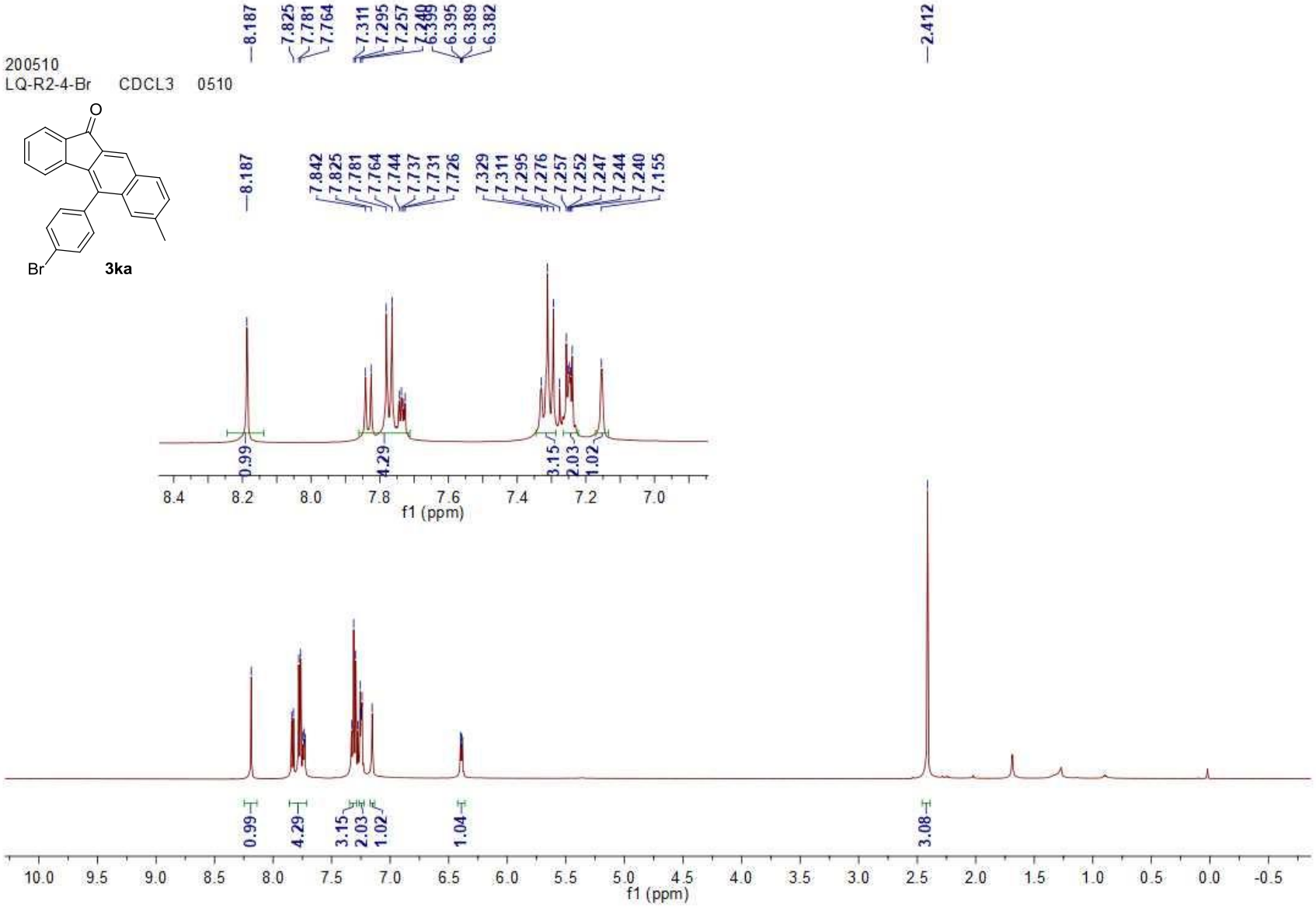
10
0
-10
f1 (ppm)


200510
LQ-R2-4-Br CDCL3 0510
Br
3ka
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7.295
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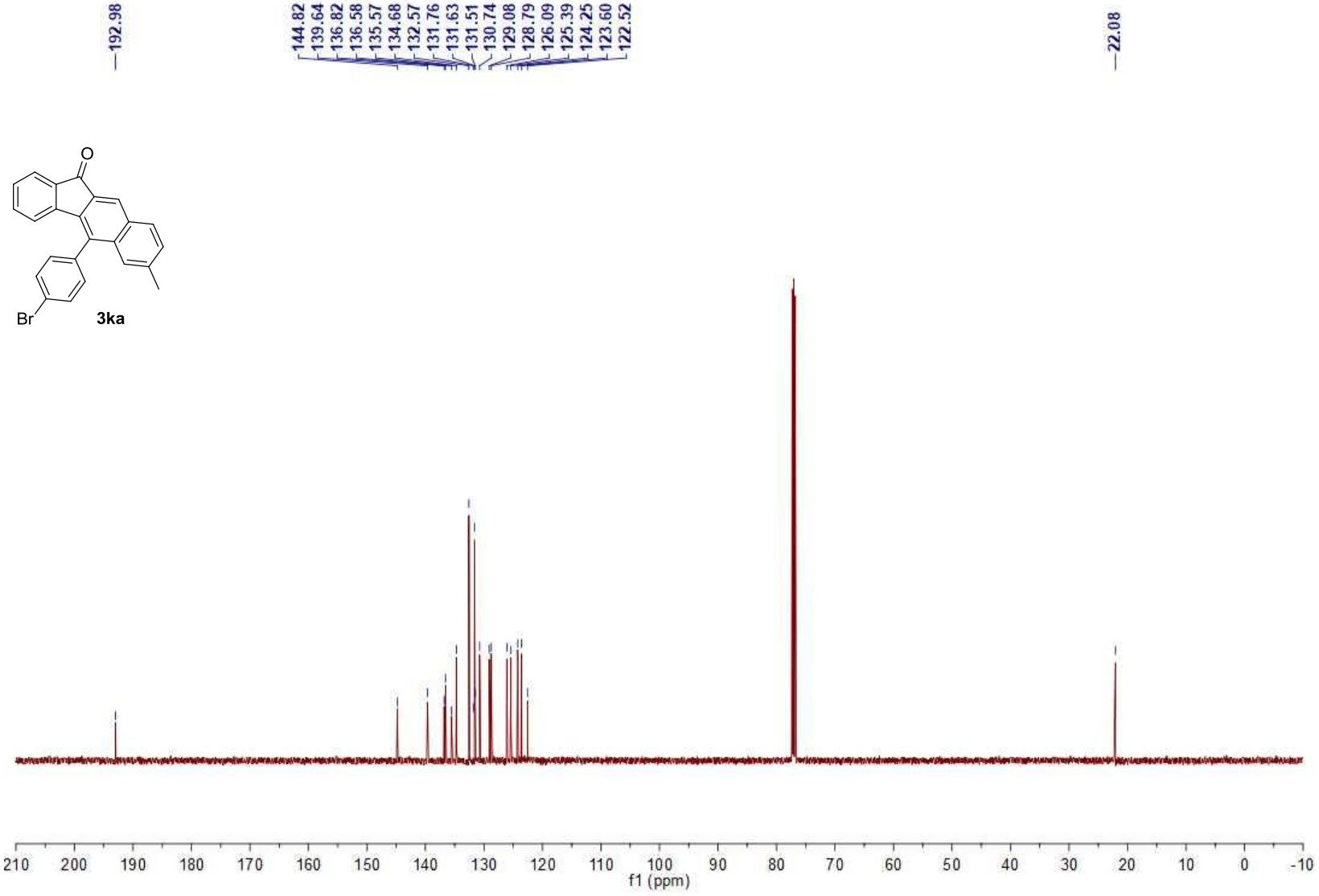
6.395
6.389
6.382
2.412
7.842
7.825
7.781
7.764
7.744
7.737
7.731
7.726
7.329
7.311
7.295
7.276
7.257
7.252
7.247
7.244
7.240
7.155
0.99
4.29
3.15
2.03
1.02
1.04
3.08
f1 (ppm)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144.82
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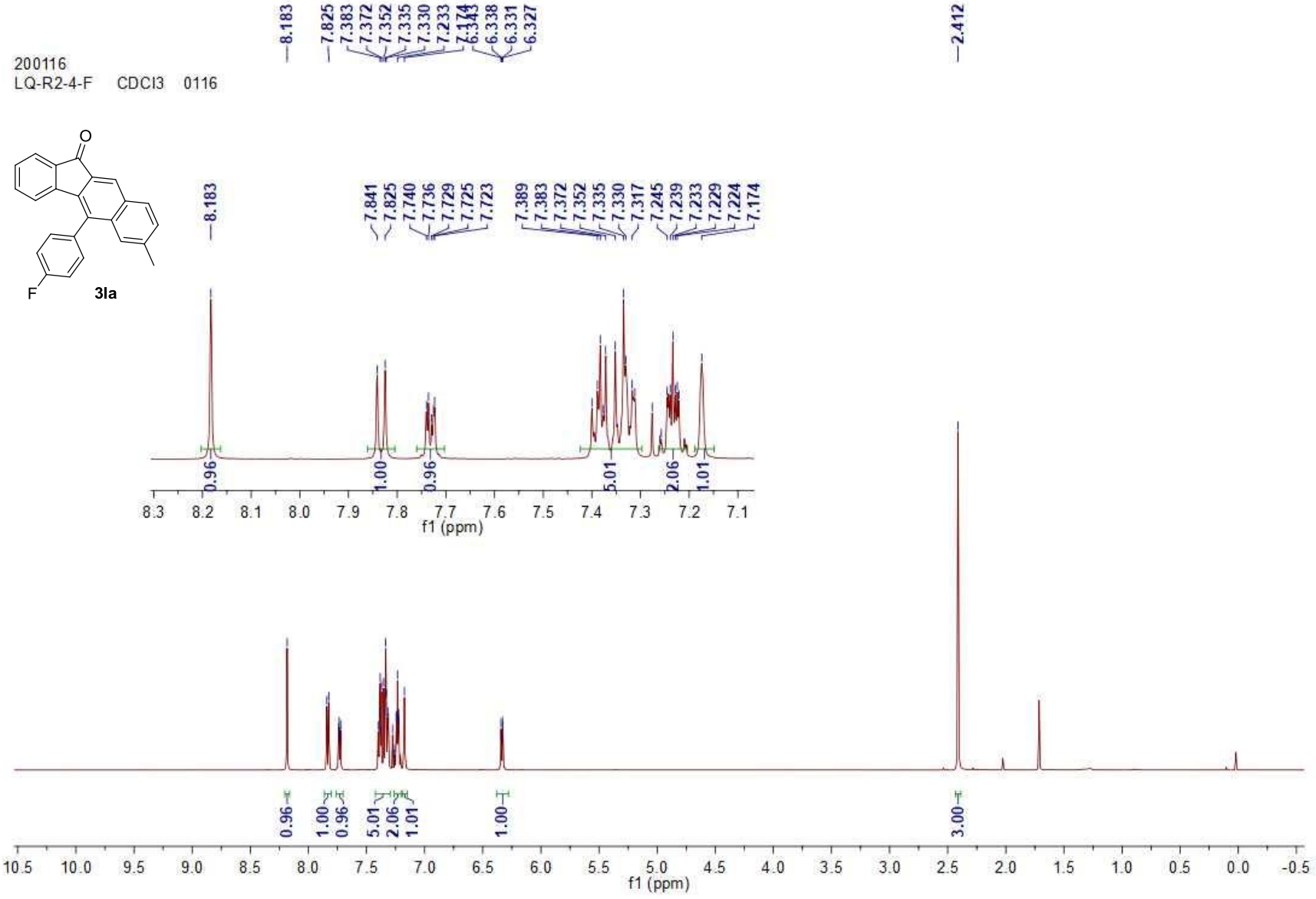
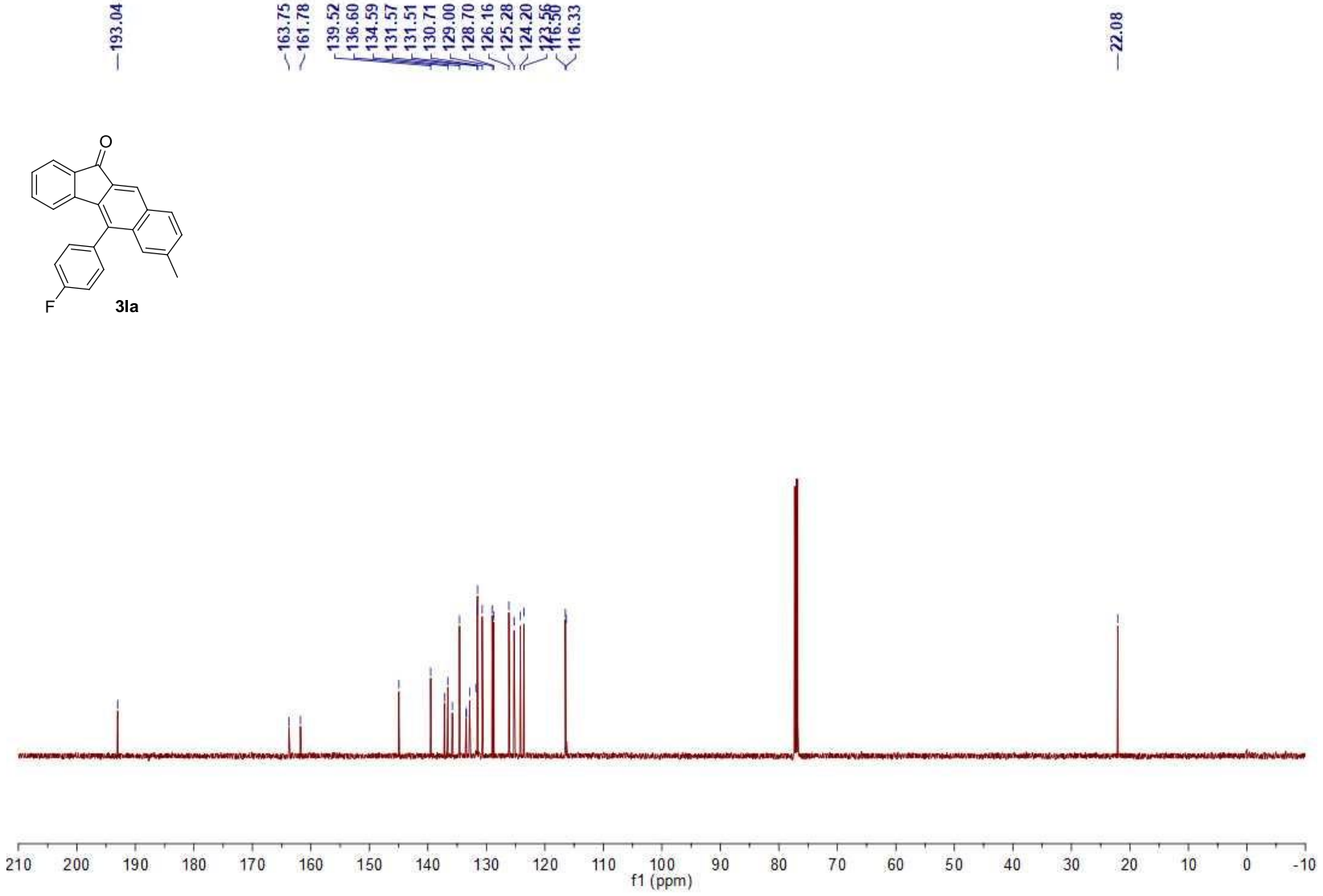
136.82
136.58
135.57
134.68
132.57
131.76
131.63
131.51
130.74
129.08
128.79
126.09
125.39
124.25
123.60
122.52
22.08
O
Br
3ka
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


200116
LQ-R2-4-F CDCl3 0116
3la
8.183
7.825
7.383
7.372
7.352
7.335
7.330
7.233
7.174
6.343
6.338
6.331
6.327
2.412
f1 (ppm)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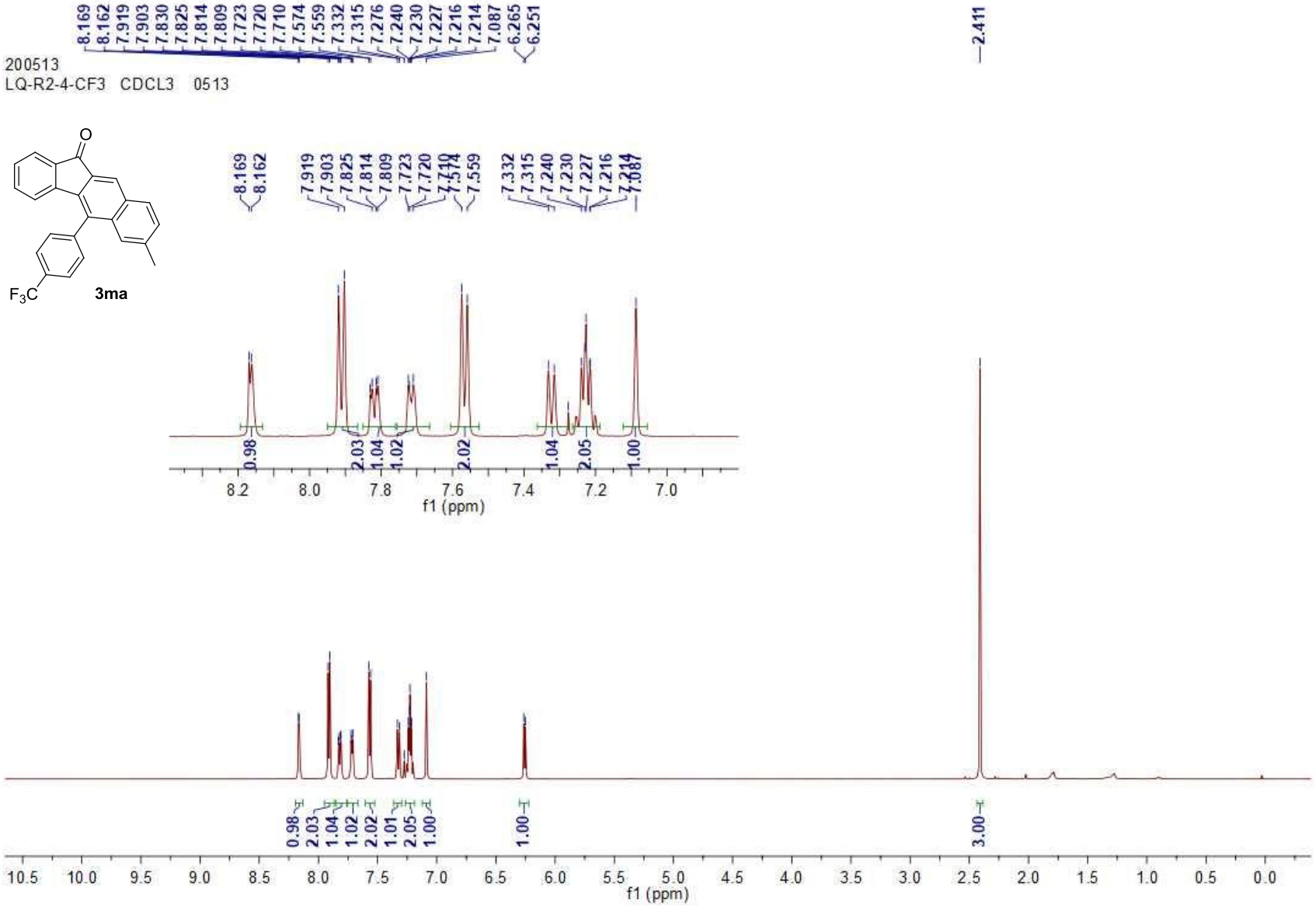
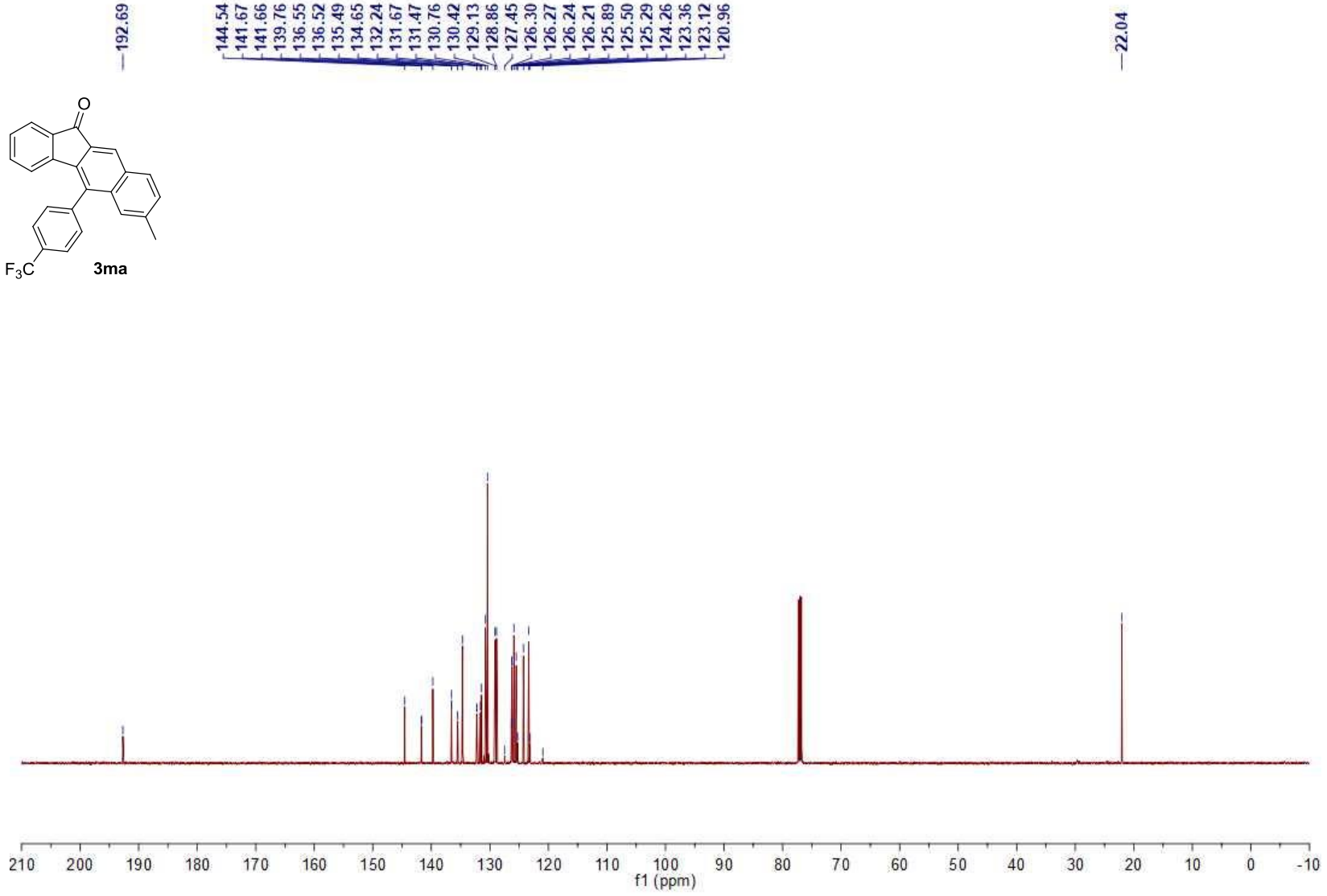
163.75
161.78
139.52
136.60
134.59
131.57
131.51
130.71
129.00
128.70
126.16
125.28
124.20
116.33
22.08
O
F
3la
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


200513
LQ-R2-4-CF3 CDCL3 0513
3ma
f1 (ppm)


192.69
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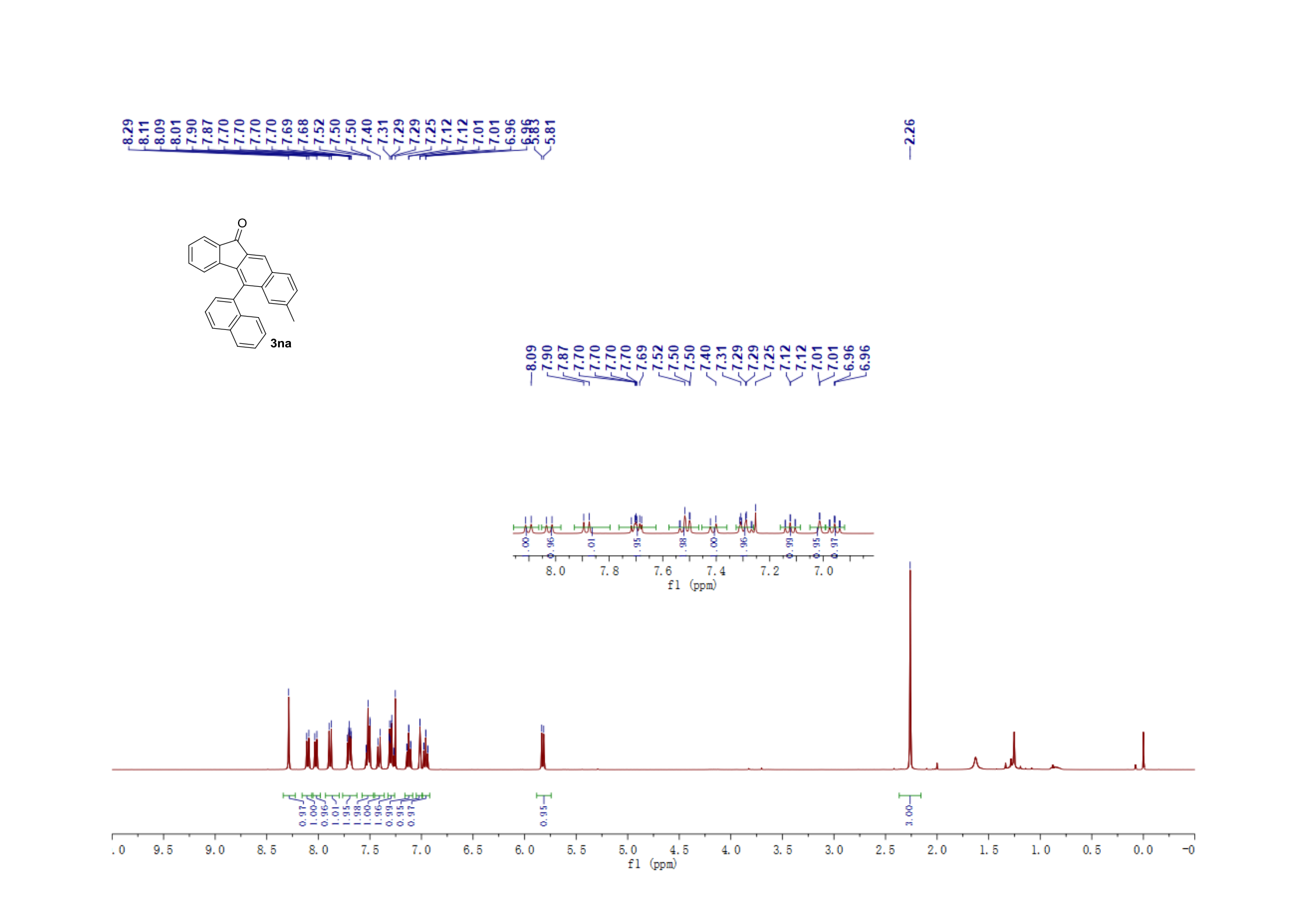
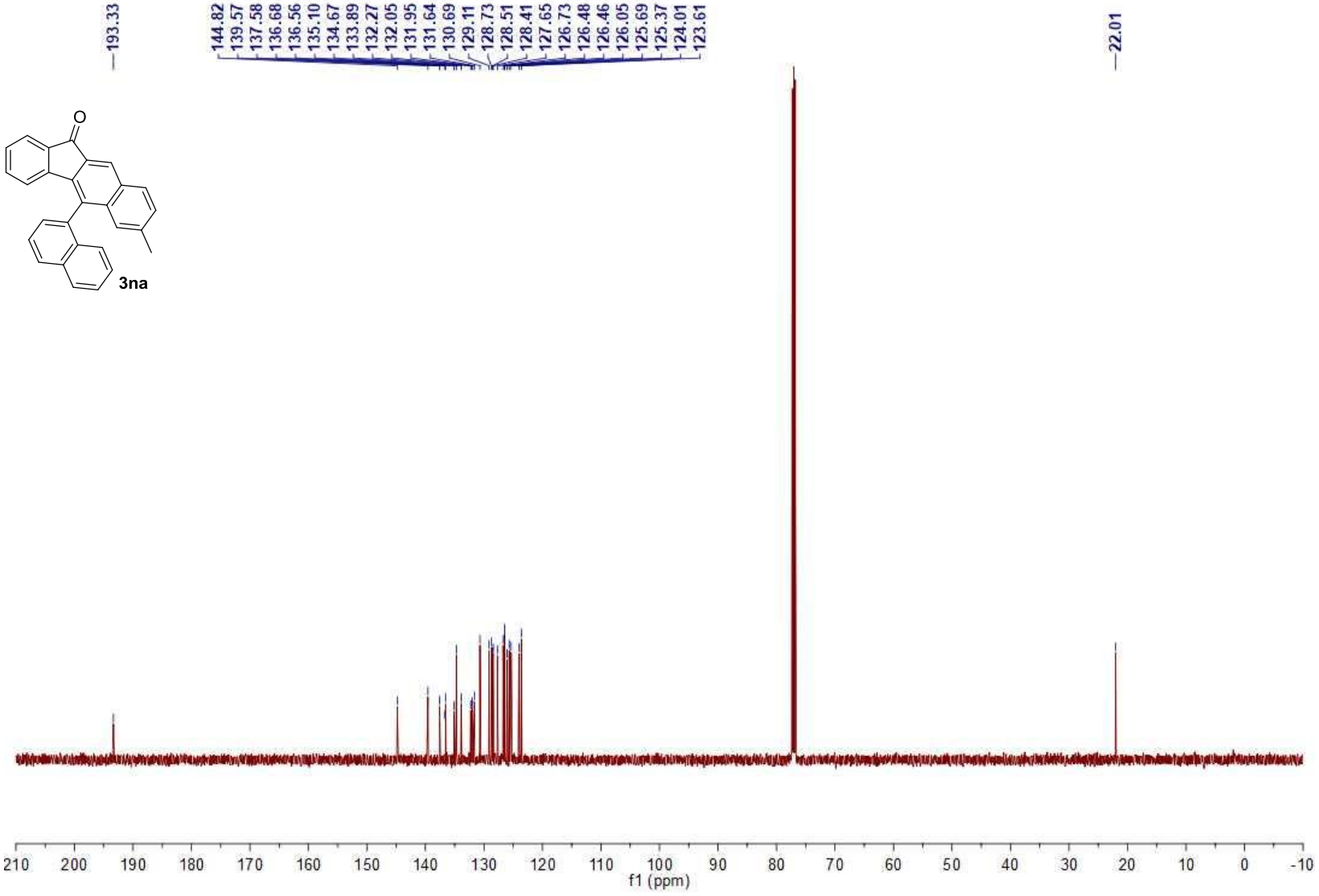
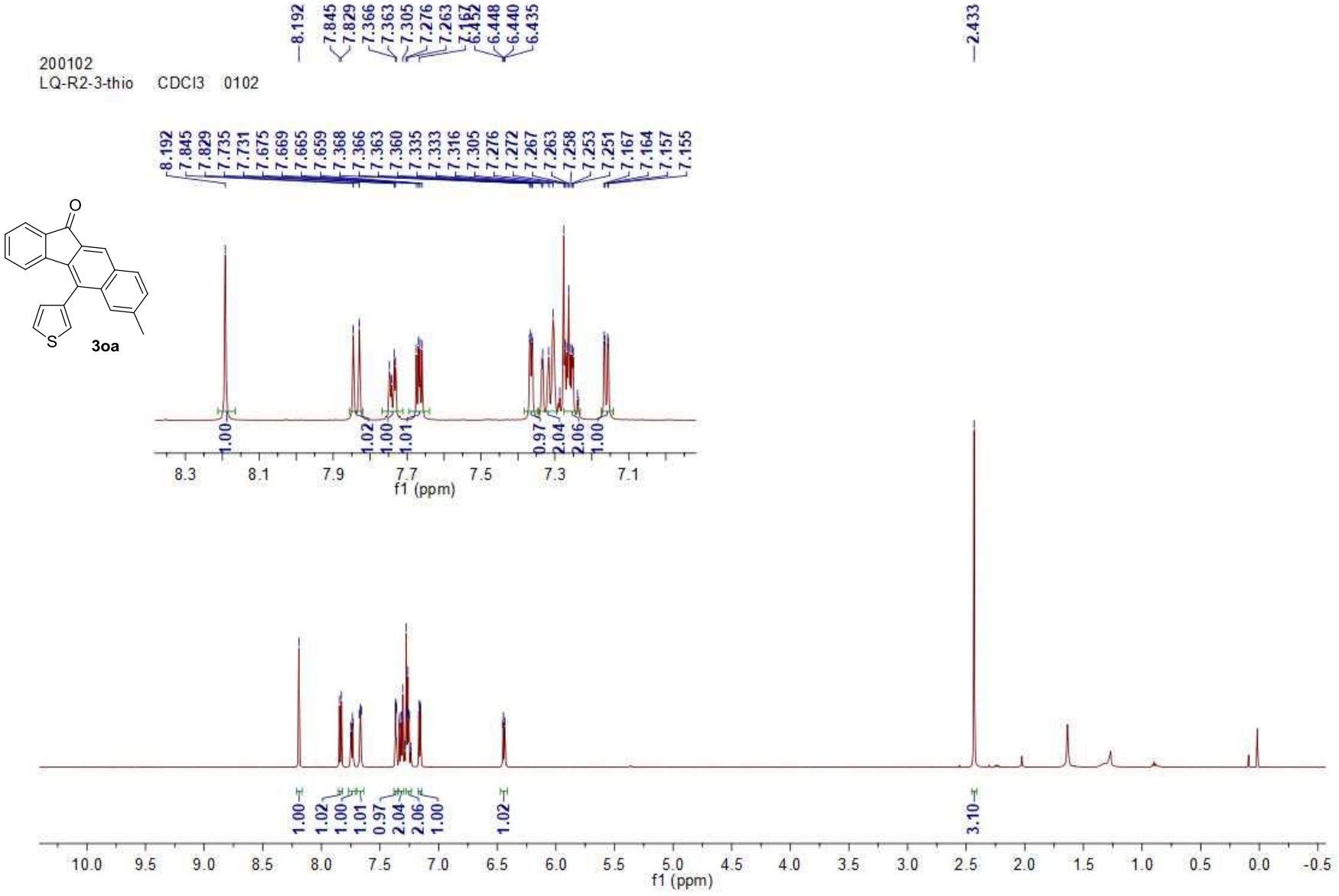
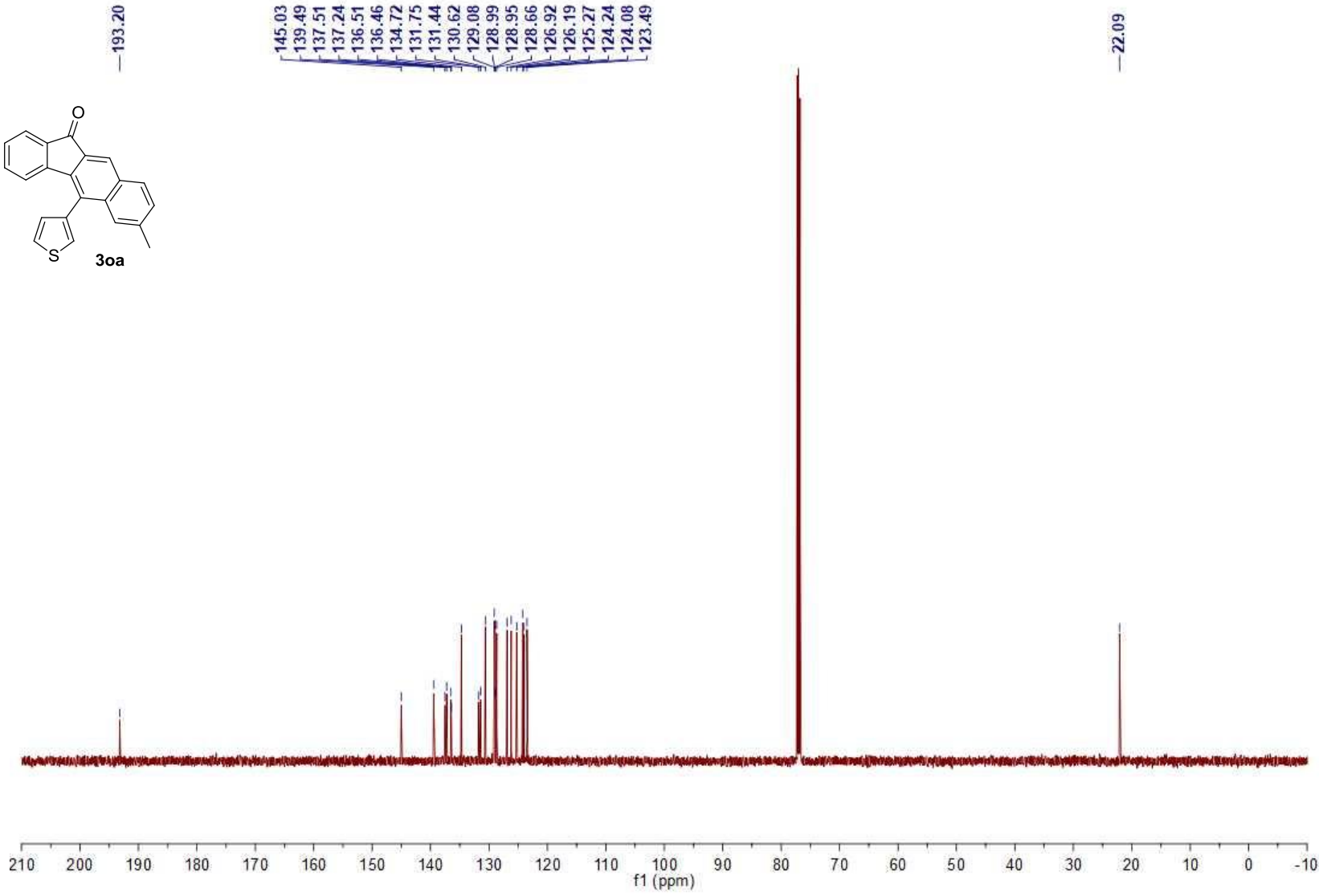
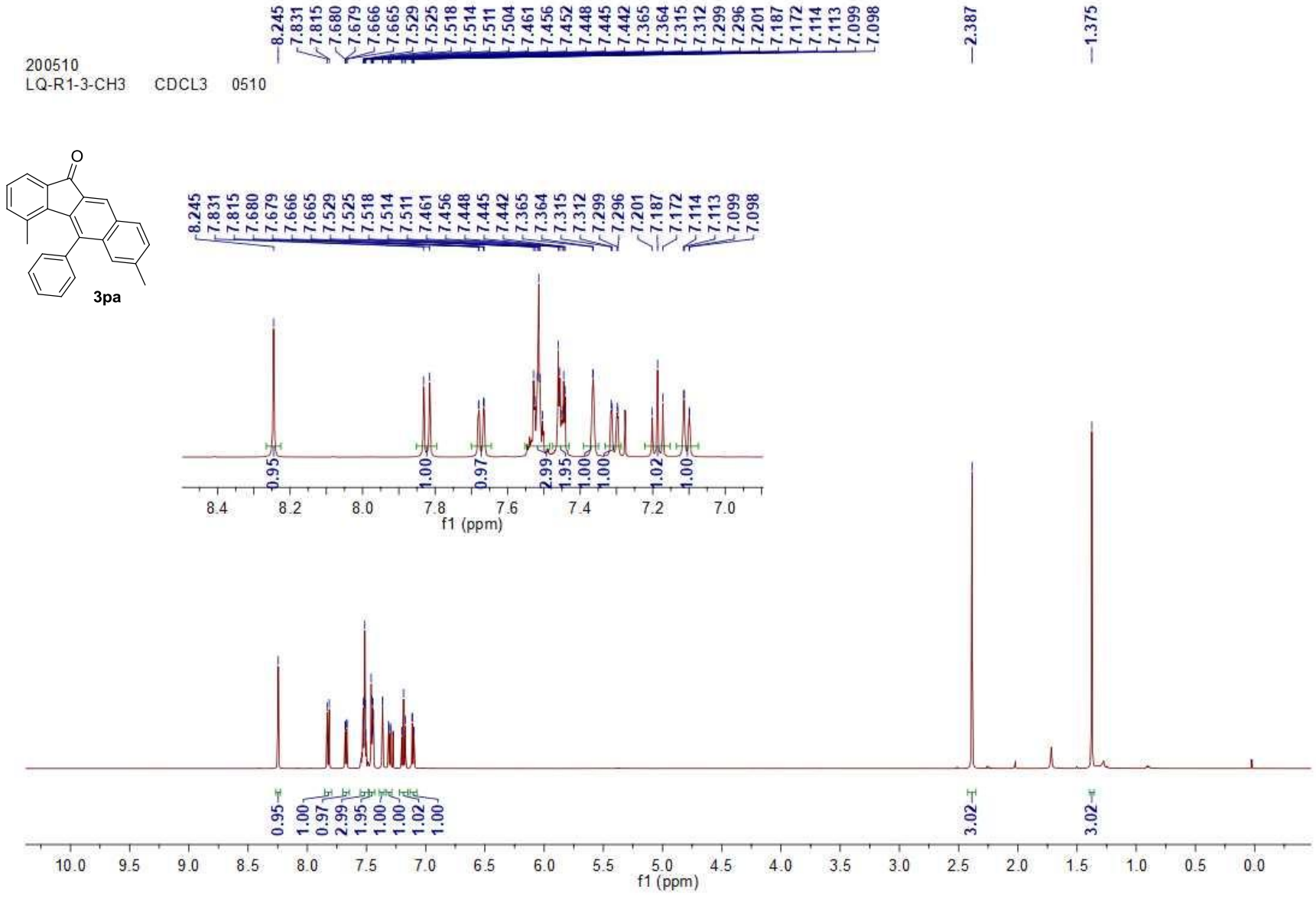
141.67
141.66
139.76
136.55
136.52
135.49
134.65
132.24
131.67
131.47
130.76
130.42
129.13
128.86
127.45
126.30
126.27
126.24
126.21
125.89
125.50
125.29
124.26
123.36
123.12
120.96
22.04
O
F3C
3ma
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

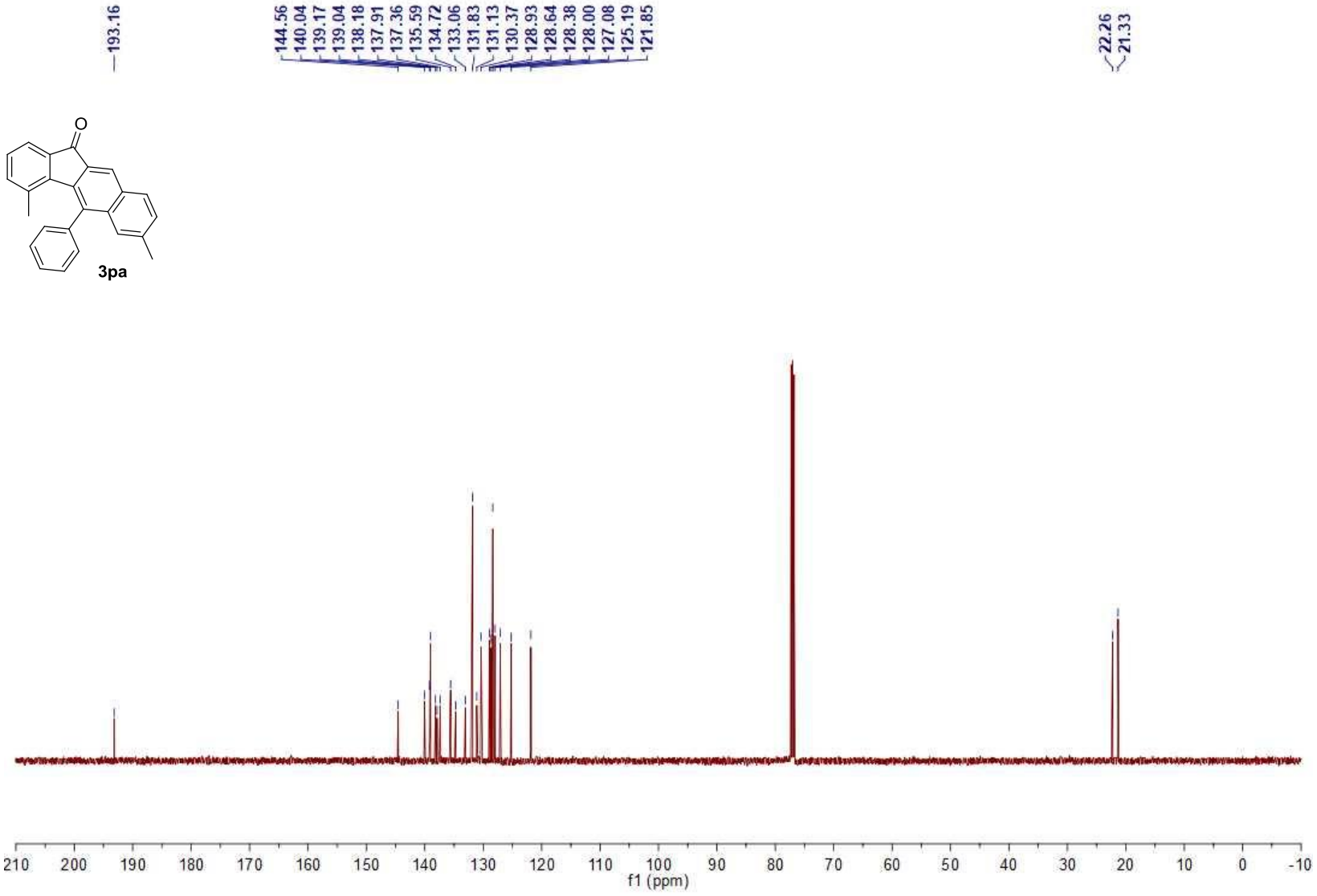

8.29
8.11
8.09
8.01
7.90
7.87
7.70
7.70
7.70
7.70
7.69
7.68
7.52
7.50
7.50
7.40
7.31
7.29
7.29
7.25
7.12
7.12
7.01
7.01
6.96
6.96
5.83
5.81
2.26
O
3na
8.09
7.90
7.87
7.70
7.70
7.70
7.70
7.69
7.52
7.50
7.50
7.40
7.31
7.29
7.29
7.25
7.12
7.12
7.01
7.01
6.96
6.96
8.0
7.8
7.6
7.4
7.2
7.0
f1 (ppm)
0.97
1.00
0.96
1.01
1.95
1.98
1.00
1.96
0.99
0.95
0.97
0.95
3.00
.0
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
−0
f1 (ppm)

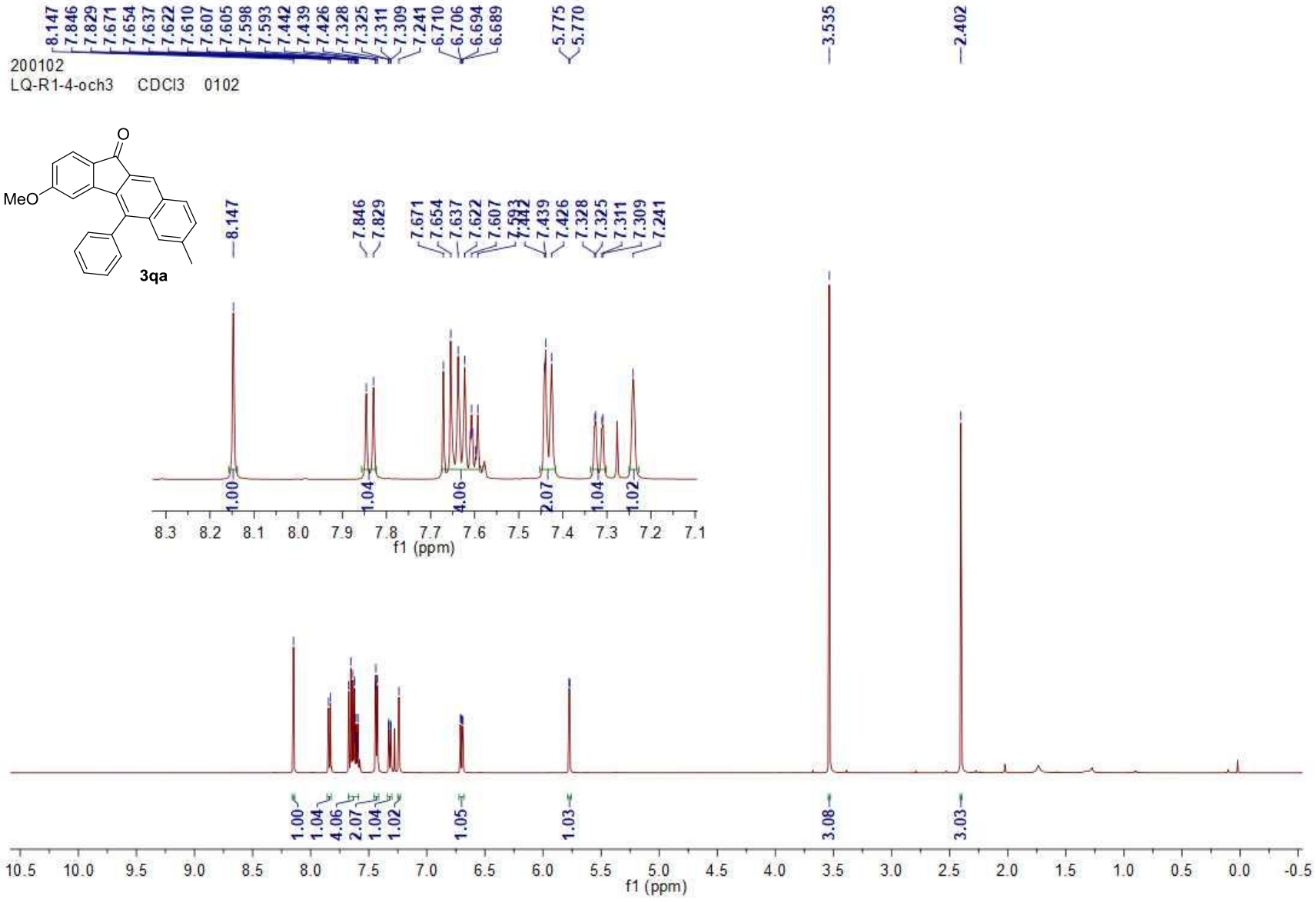

193.33
144.82
139.57
137.58
136.68
136.56
135.10
134.67
133.89
132.27
132.05
131.95
131.64
130.69
129.11
128.73
128.51
128.41
127.65
126.73
126.48
126.46
126.05
125.69
125.37
124.01
123.61
22.01
O
3na
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

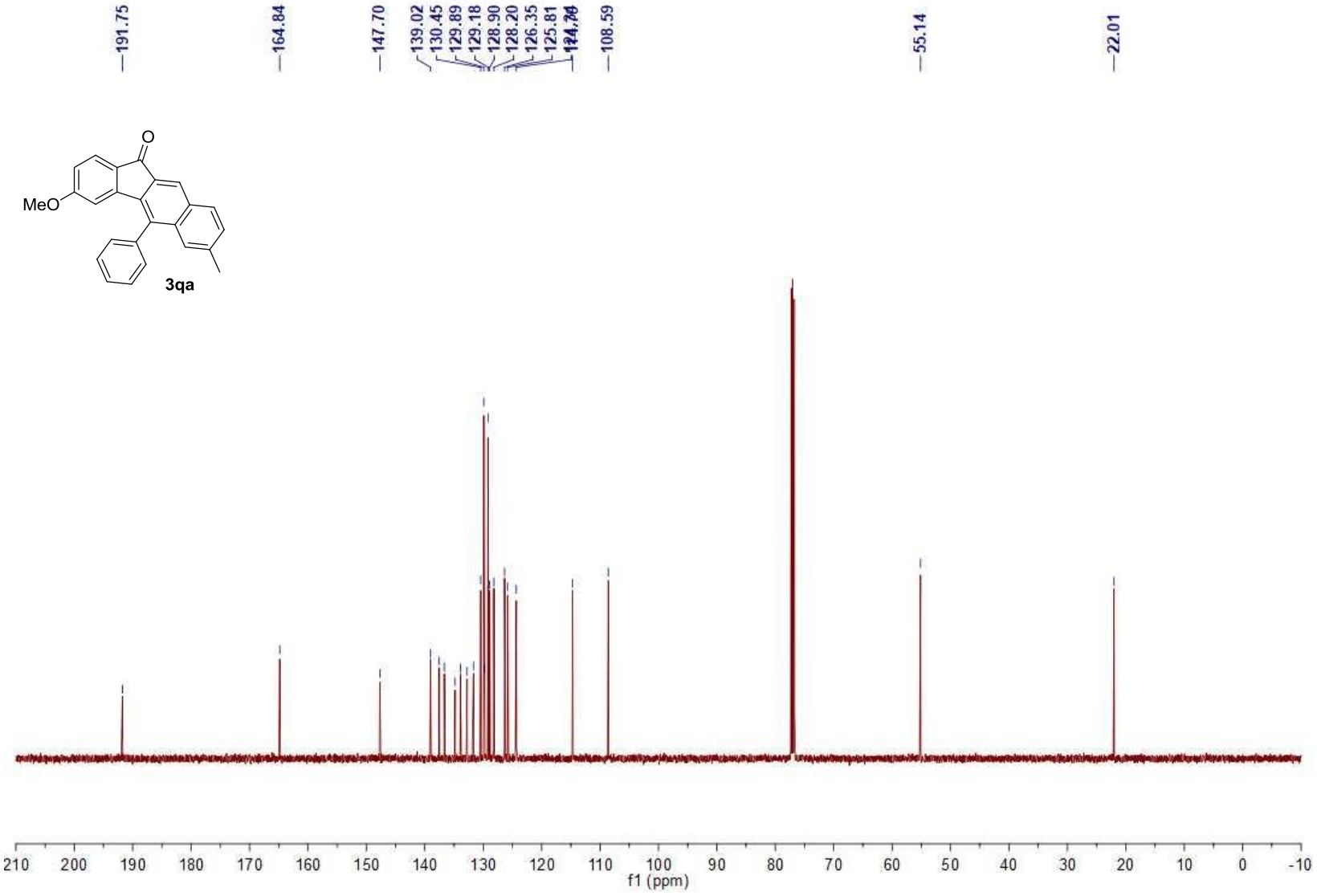

200102
LQ-R2-3-thio CDCl3 0102
8.192
7.845
7.829
7.366
7.363
7.305
7.276
7.263
6.448
6.440
6.435
2.433
O
S
3oa
f1 (ppm)

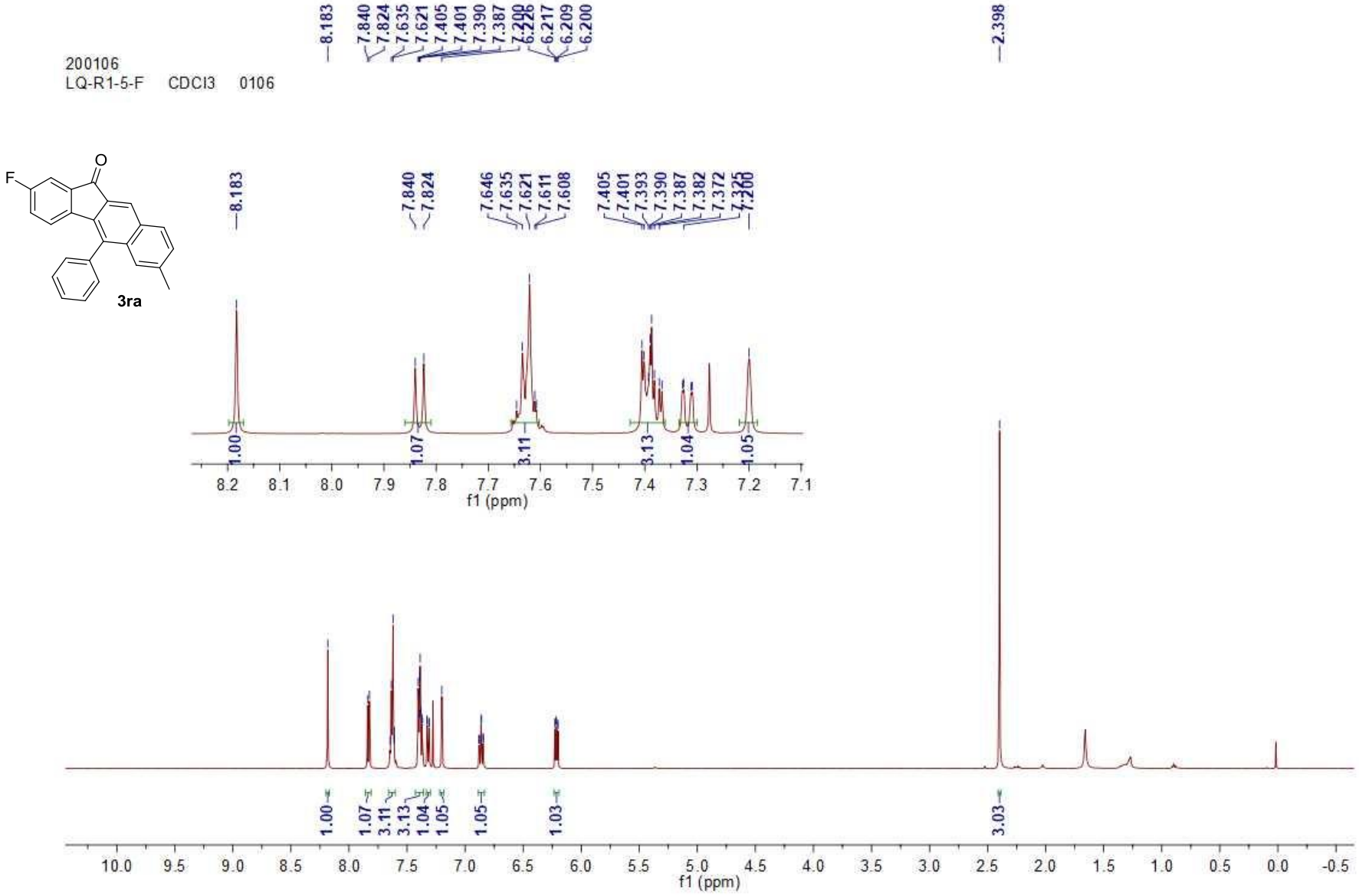

193.20
145.03
139.49
137.51
137.24
136.51
136.46
134.72
131.75
131.44
130.62
129.08
128.99
128.95
128.66
126.92
126.19
125.27
124.24
124.08
123.49
22.09
O
S
3oa
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.245
7.831
7.815
7.680
7.679
7.666
7.665
7.529
7.525
7.518
7.514
7.511
7.504
7.461
7.456
7.452
7.448
7.445
7.442
7.365
7.364
7.315
7.312
7.299
7.296
7.201
7.187
7.172
7.114
7.113
7.099
7.098
2.387
1.375
200510
LQ-R1-3-CH3 CDCL3 0510
O
3pa
0.95
1.00
0.97
2.99
1.95
1.00
1.00
1.02
1.00
3.02
3.02
f1 (ppm)


193.16
144.56
140.04
139.17
139.04
138.18
137.91
137.36
135.59
134.72
133.06
131.83
131.13
130.37
128.93
128.64
128.38
128.00
127.08
125.19
121.85
22.26
21.33
O
3pa
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.147
7.846
7.829
7.671
7.654
7.637
7.622
7.610
7.607
7.605
7.598
7.593
7.442
7.439
7.426
7.328
7.325
7.311
7.309
7.241
6.710
6.706
6.694
6.689
5.775
5.770
3.535
2.402
200102
LQ-R1-4-och3 CDCl3 0102
MeO
O
3qa
f1 (ppm)


191.75
164.84
147.70
139.02
130.45
129.89
129.18
128.90
128.20
126.35
125.81
108.59
55.14
22.01
O
MeO
3qa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


200106
LQ-R1-5-F CDCl3 0106
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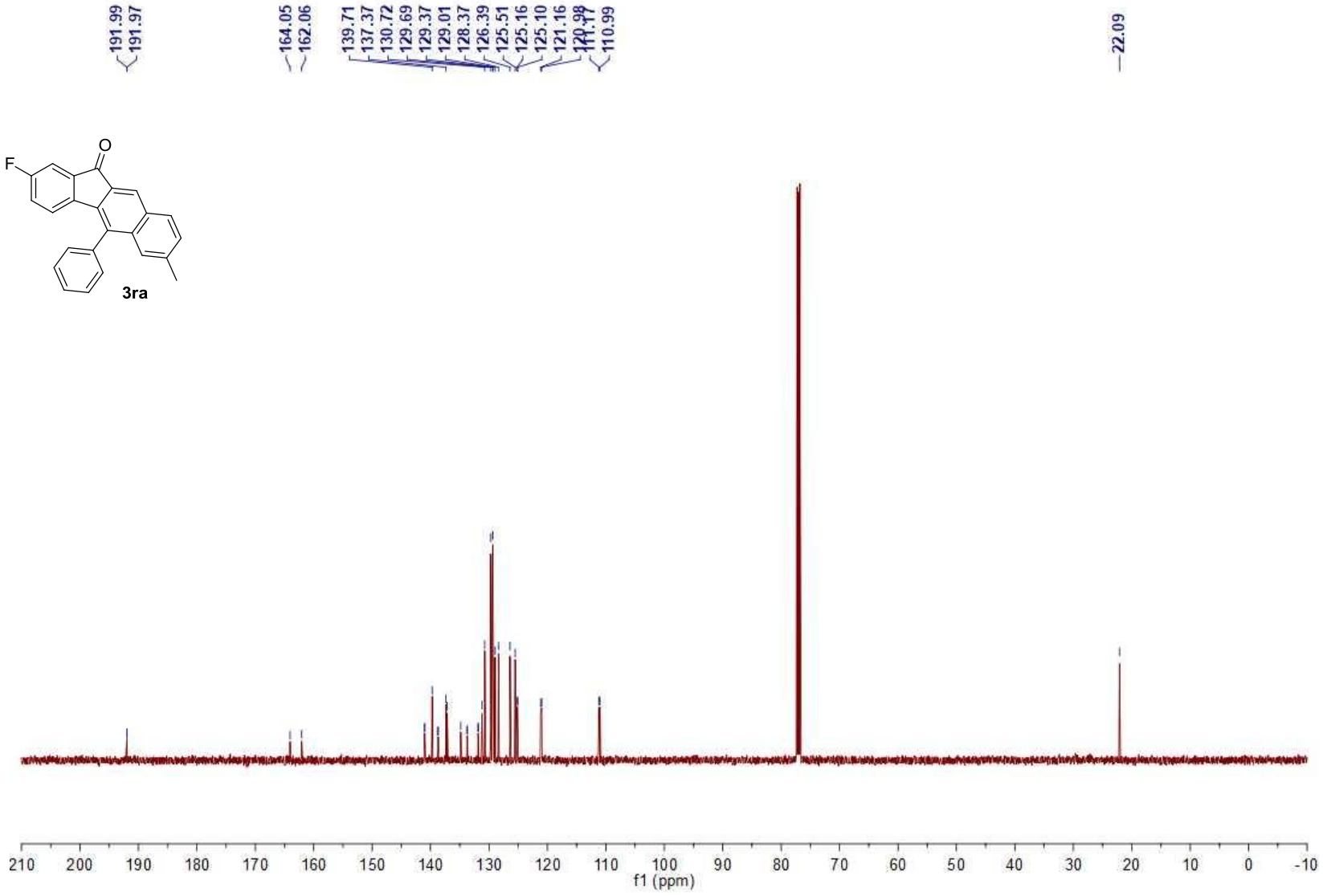
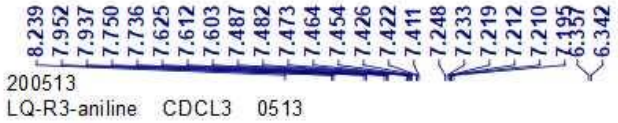
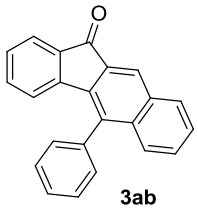
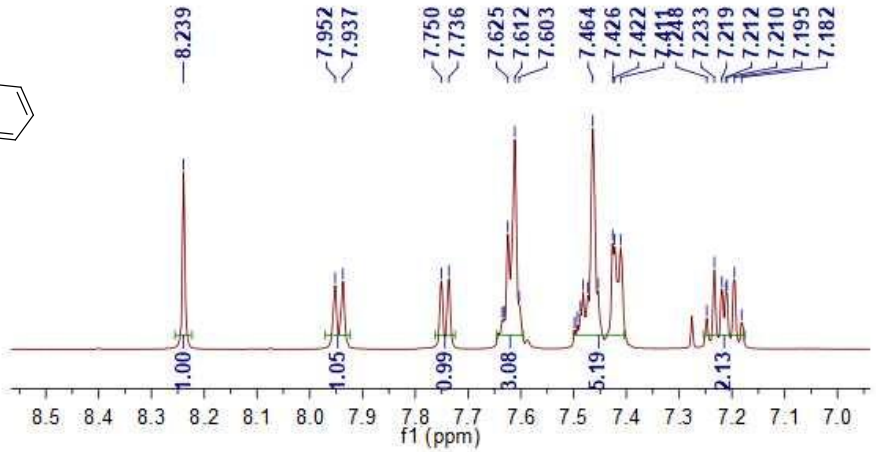
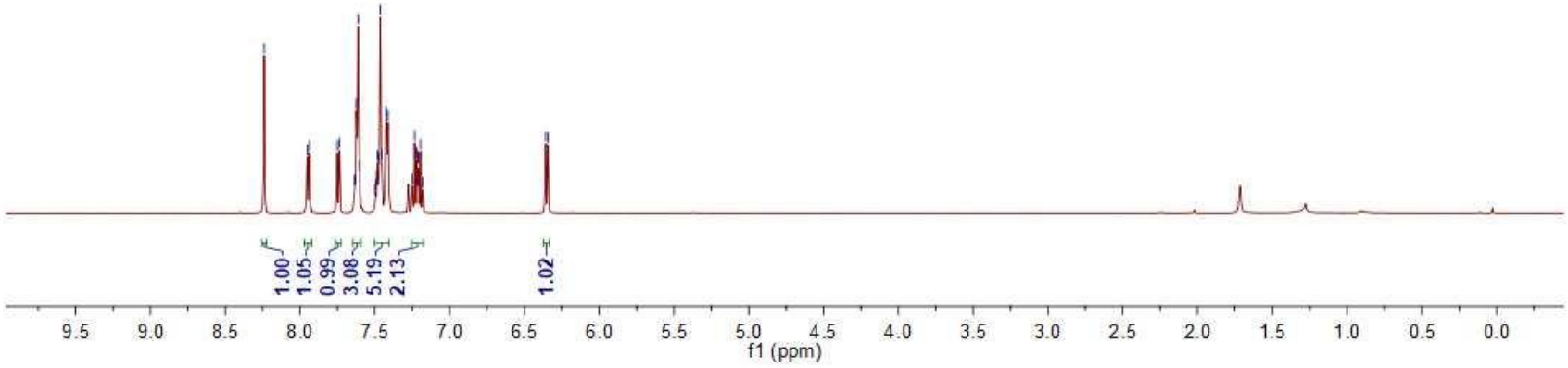
7.840
7.824
7.635
7.621
7.405
7.401
7.390
7.387
6.217
6.209
6.200
2.398
F
O
3ra
7.646
7.611
7.608
7.393
7.382
7.372
1.00
1.07
3.11
3.13
1.04
1.05
1.03
3.03
f1 (ppm)

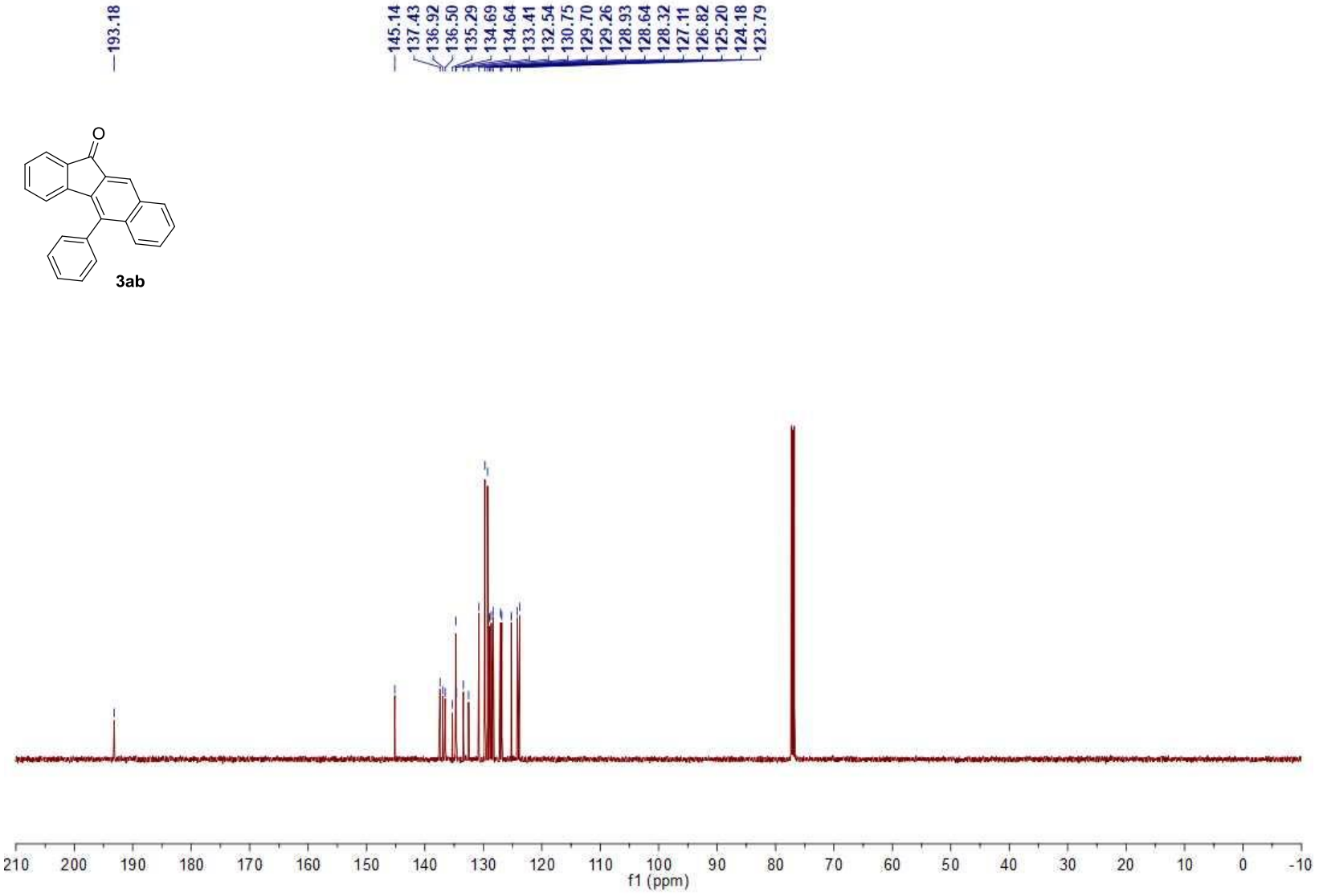

191.99
191.97
164.05
162.06
139.71
137.37
130.72
129.69
129.37
129.01
128.37
126.39
125.51
125.16
125.10
121.16
110.99
22.09
O
F
3ra
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

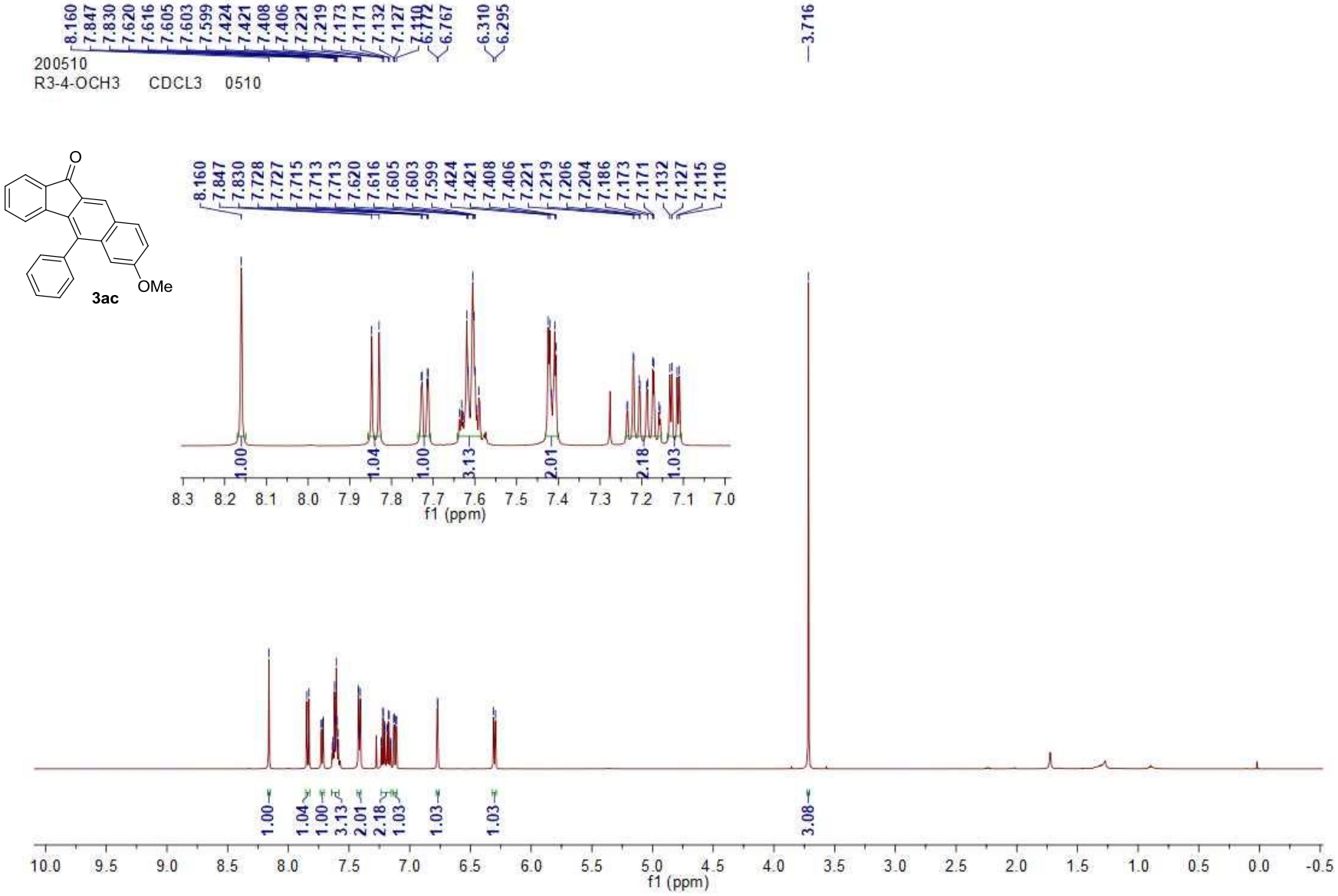

8.239
7.952
7.937
7.750
7.736
7.625
7.612
7.603
7.487
7.482
7.473
7.464
7.454
7.426
7.422
7.411
7.248
7.233
7.219
7.212
7.210
7.195
6.357
6.342
200513
LQ-R3-aniline CDCL3 0513

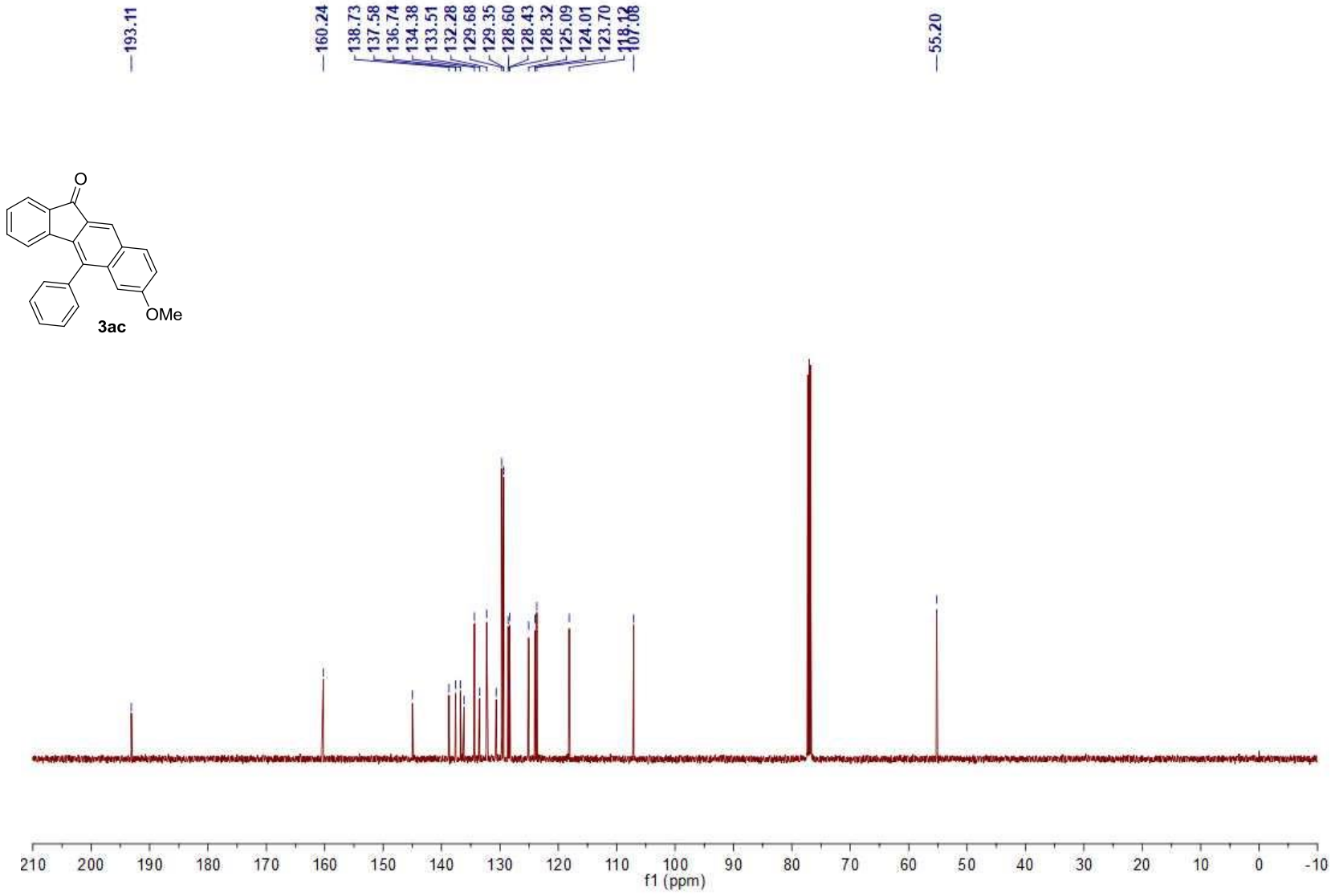

O
3ab


8.239
7.952
7.937
7.750
7.736
7.625
7.612
7.603
7.464
7.426
7.422
7.411
7.248
7.233
7.219
7.212
7.210
7.195
7.182
1.00
1.05
0.99
3.08
5.19
2.13
8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)


1.00
1.05
0.99
3.08
5.19
2.13
1.02
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)


193.18
145.14
137.43
136.92
136.50
135.29
134.69
134.64
133.41
132.54
130.75
129.70
129.26
128.93
128.64
128.32
127.11
126.82
125.20
124.18
123.79
O
3ab
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.160
7.847
7.830
7.620
7.616
7.605
7.603
7.599
7.424
7.421
7.408
7.406
7.221
7.219
7.173
7.171
7.132
7.127
7.110
6.772
6.767
6.310
6.295
3.716
200510
R3-4-OCH3 CDCL3 0510
O
OMe
3ac
8.160
7.847
7.830
7.728
7.727
7.715
7.713
7.713
7.620
7.616
7.605
7.603
7.599
7.424
7.421
7.408
7.406
7.221
7.219
7.206
7.204
7.186
7.173
7.171
7.132
7.127
7.115
7.110
1.00
1.04
1.00
3.13
2.01
2.18
1.03
8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
1.00
1.04
1.00
3.13
2.01
2.18
1.03
1.03
1.03
3.08
10.0 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 -0.5
f1 (ppm)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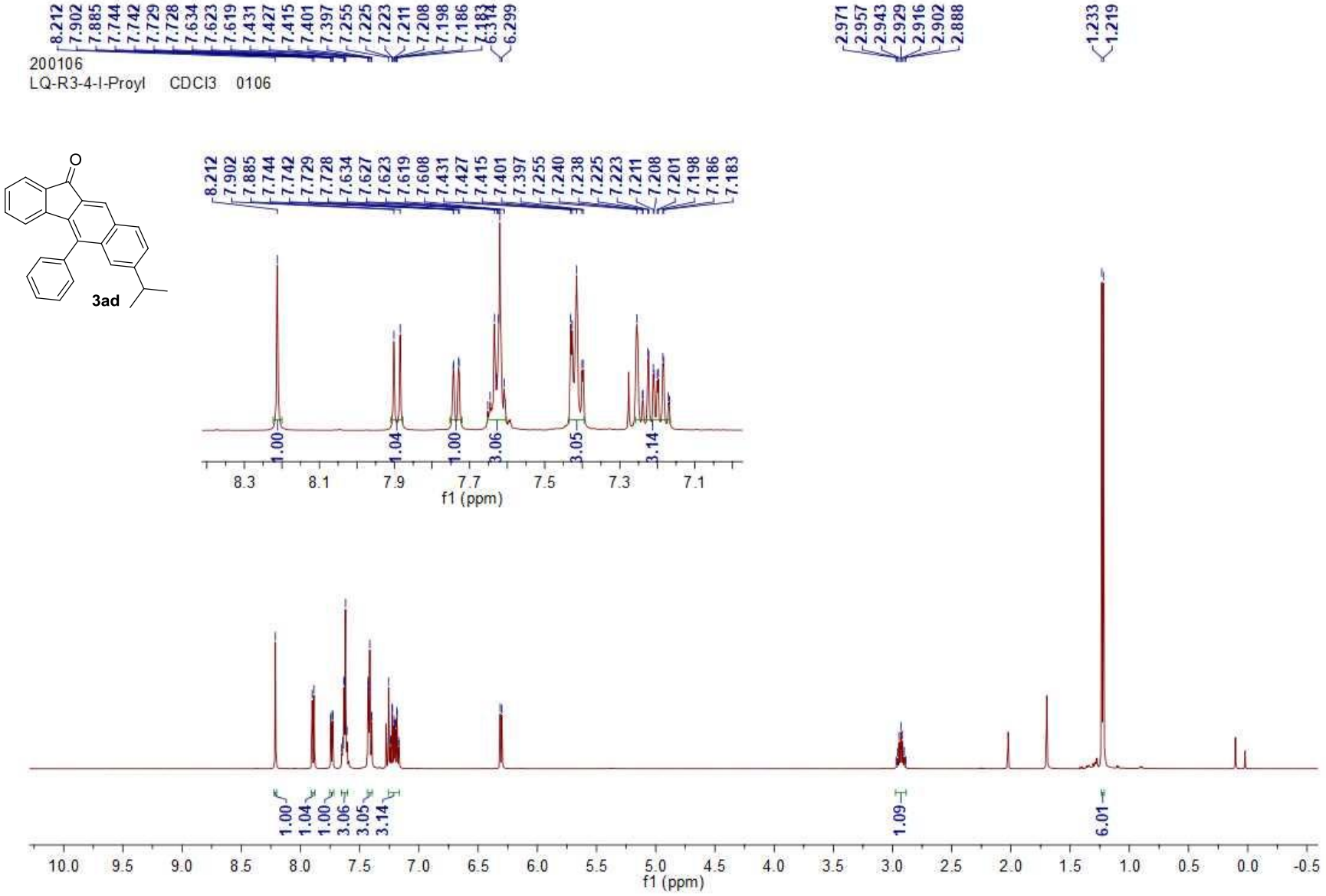
137.58
136.74
134.38
133.51
132.28
129.68
129.35
128.60
128.43
128.32
125.09
124.01
123.70
55.20
O
OMe
3ac
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.212
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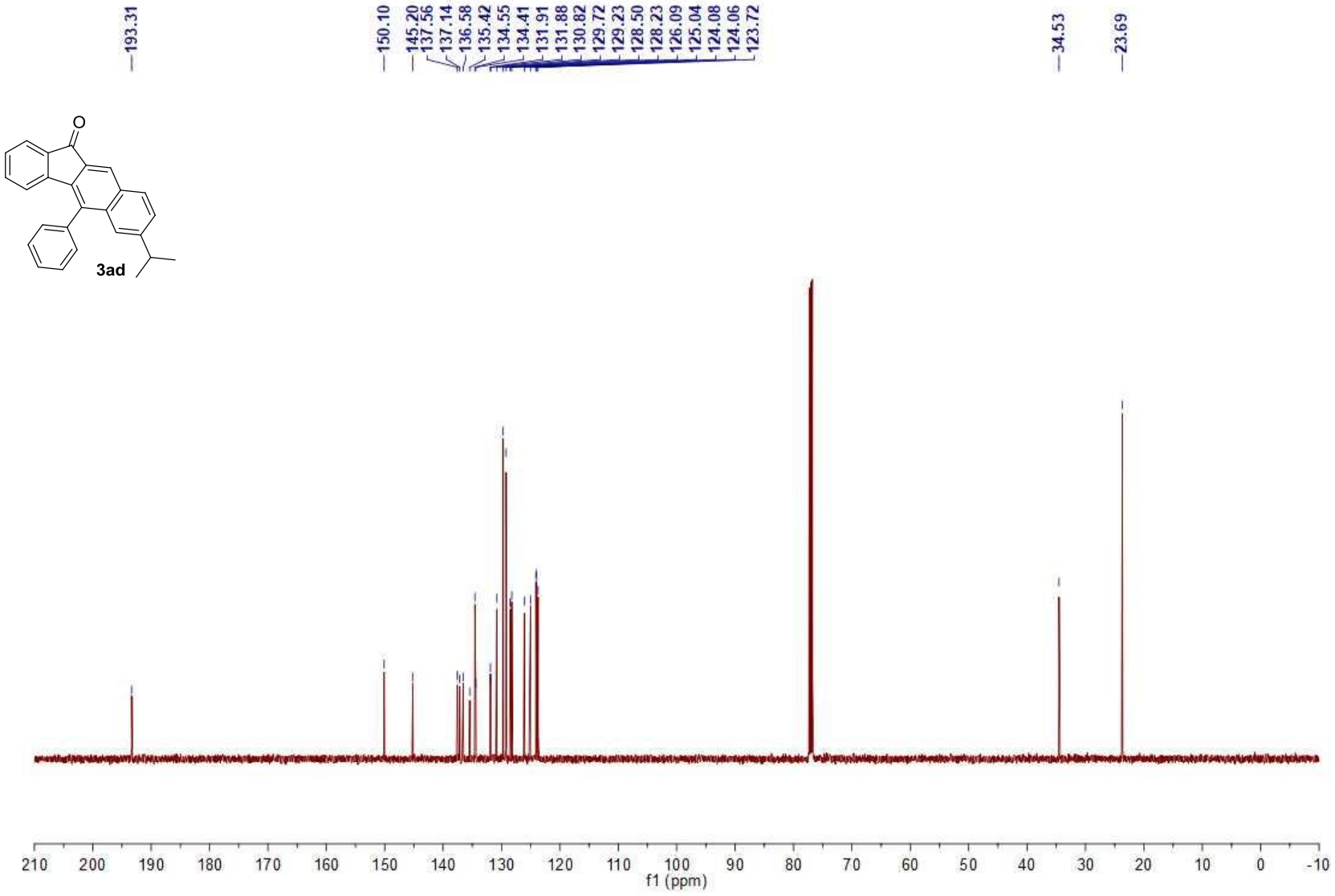
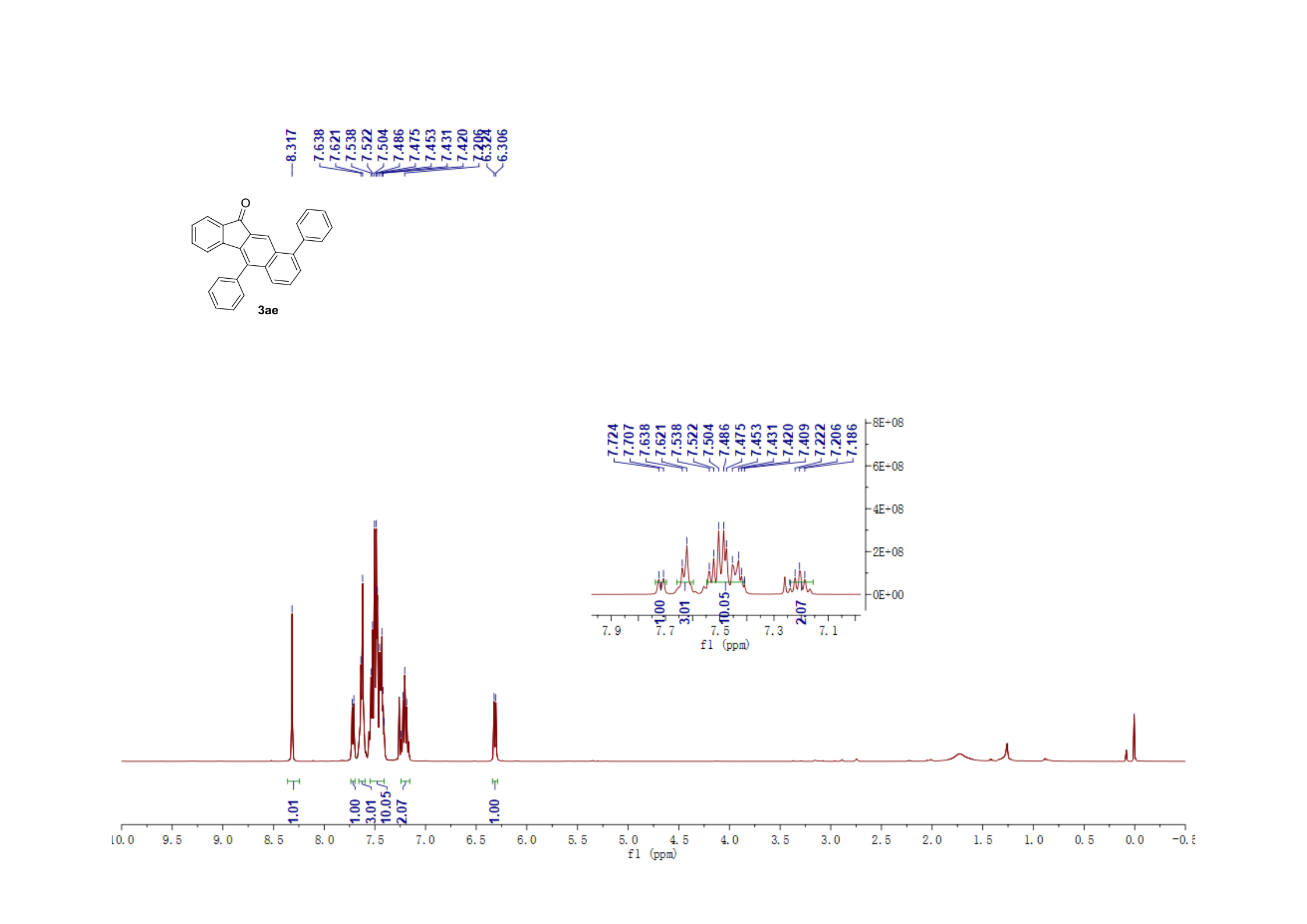
7.885
7.744
7.742
7.729
7.728
7.634
7.623
7.619
7.431
7.427
7.415
7.401
7.397
7.255
7.225
7.223
7.211
7.208
7.198
7.186
7.183
6.314
6.299
2.971
2.957
2.943
2.929
2.916
2.902
2.888
1.233
1.219
200106
LQ-R3-4-I-Proyl CDCl3 0106
3ad
1.00
1.04
1.00
3.06
3.05
3.14
1.09
6.01
f1 (ppm)


193.31
150.10
145.20
137.56
137.14
136.58
135.42
134.55
134.41
131.91
131.88
130.82
129.72
129.23
128.50
128.23
126.09
125.04
124.08
124.06
123.72
34.53
23.69
O
3ad
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.317
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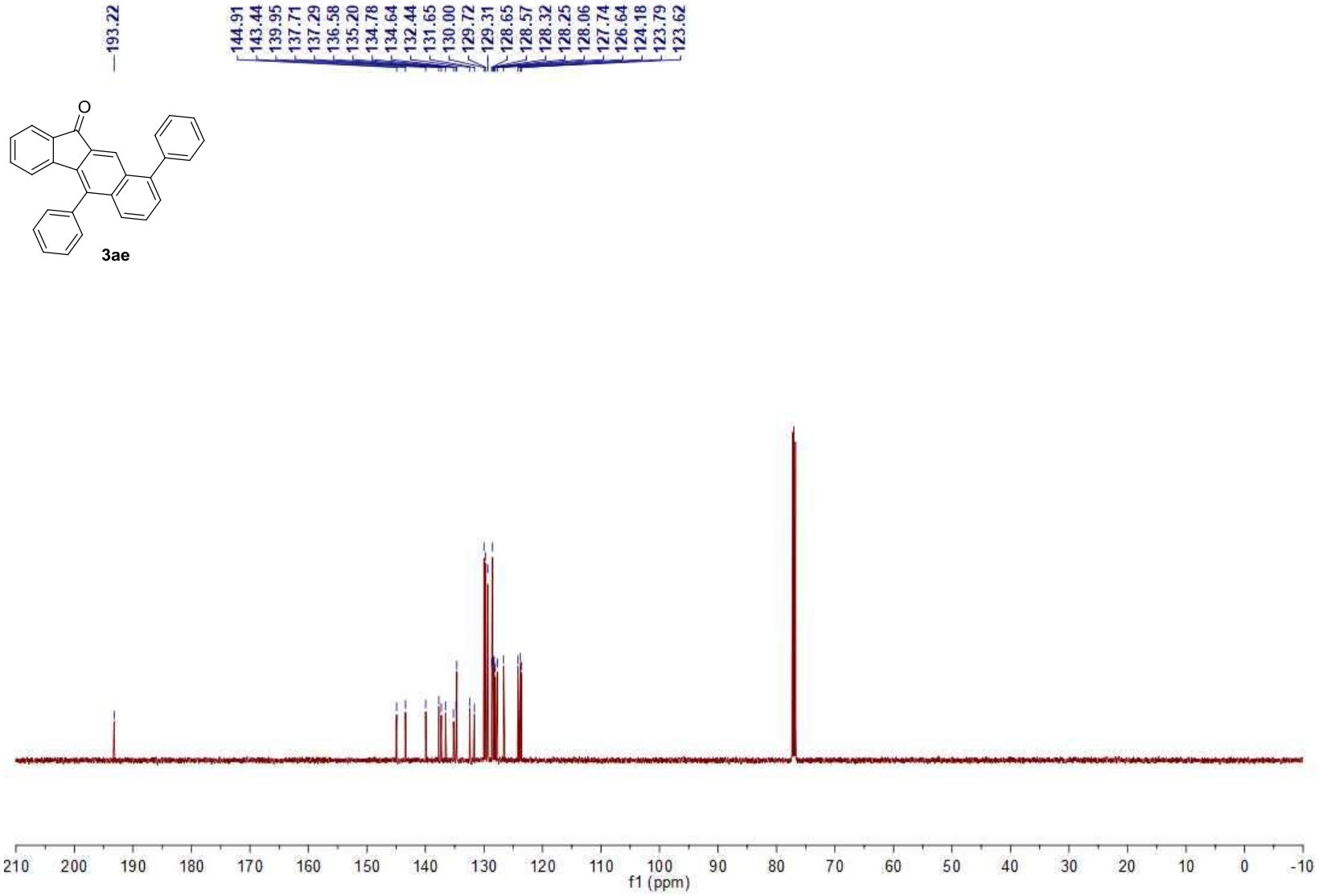
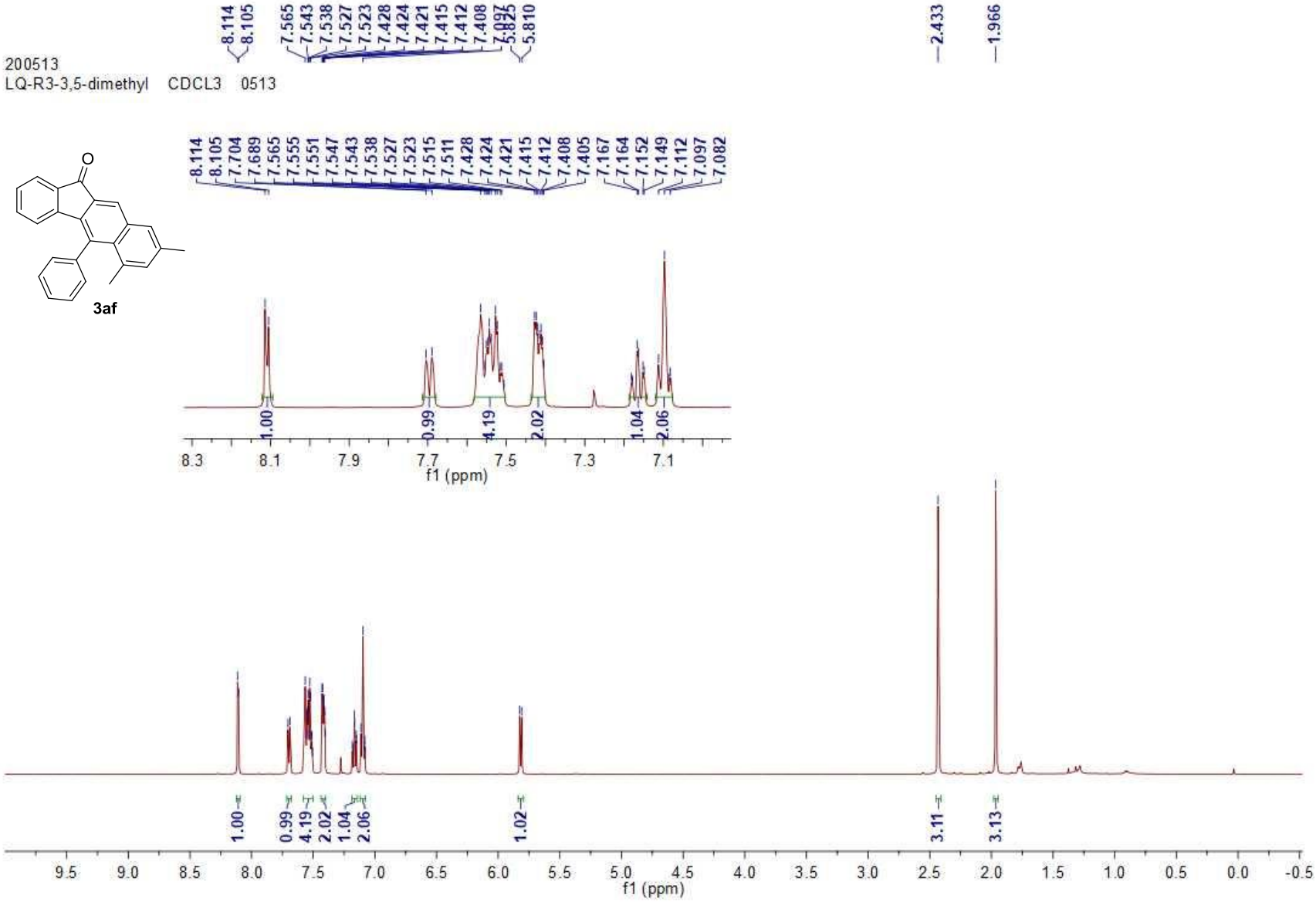
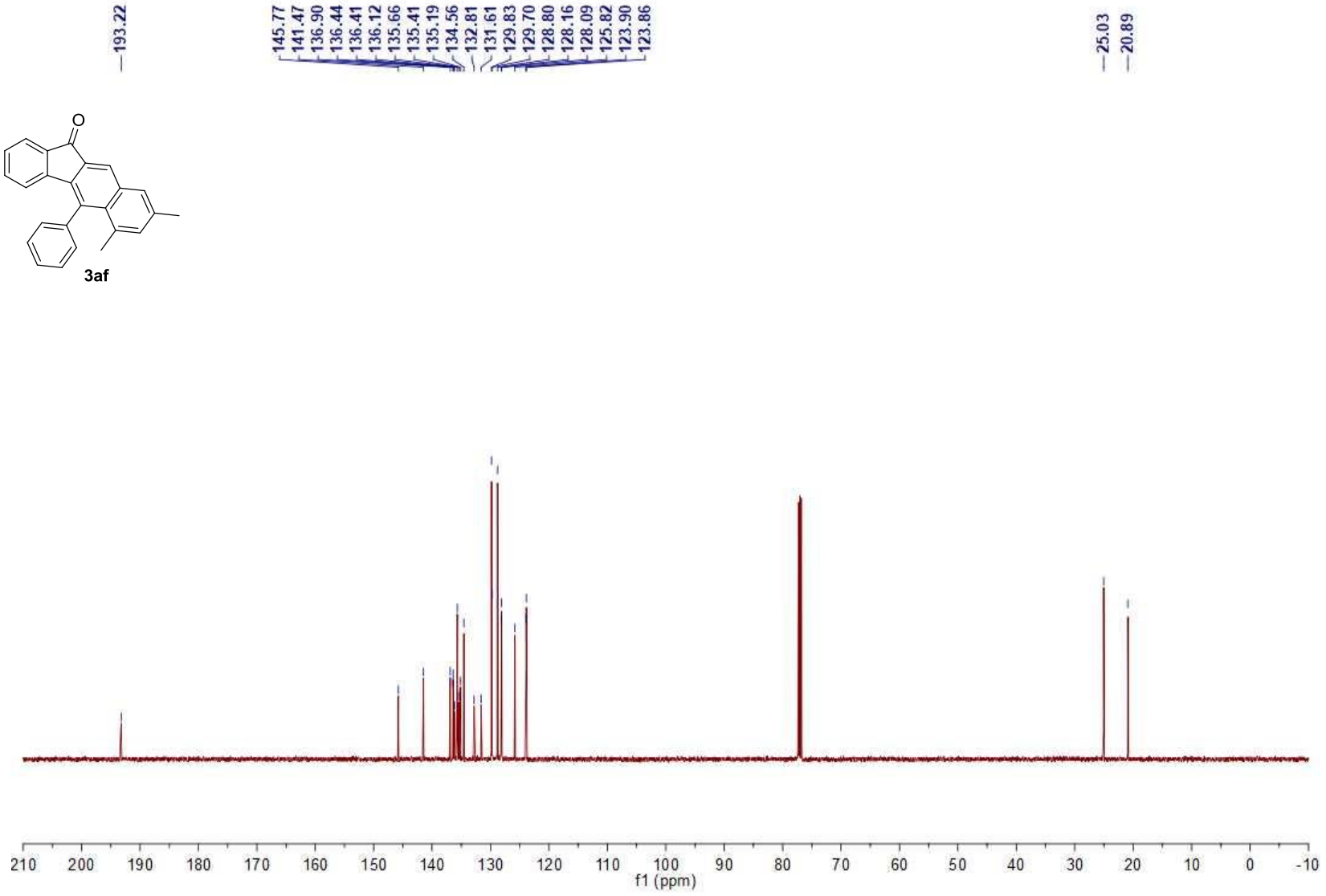
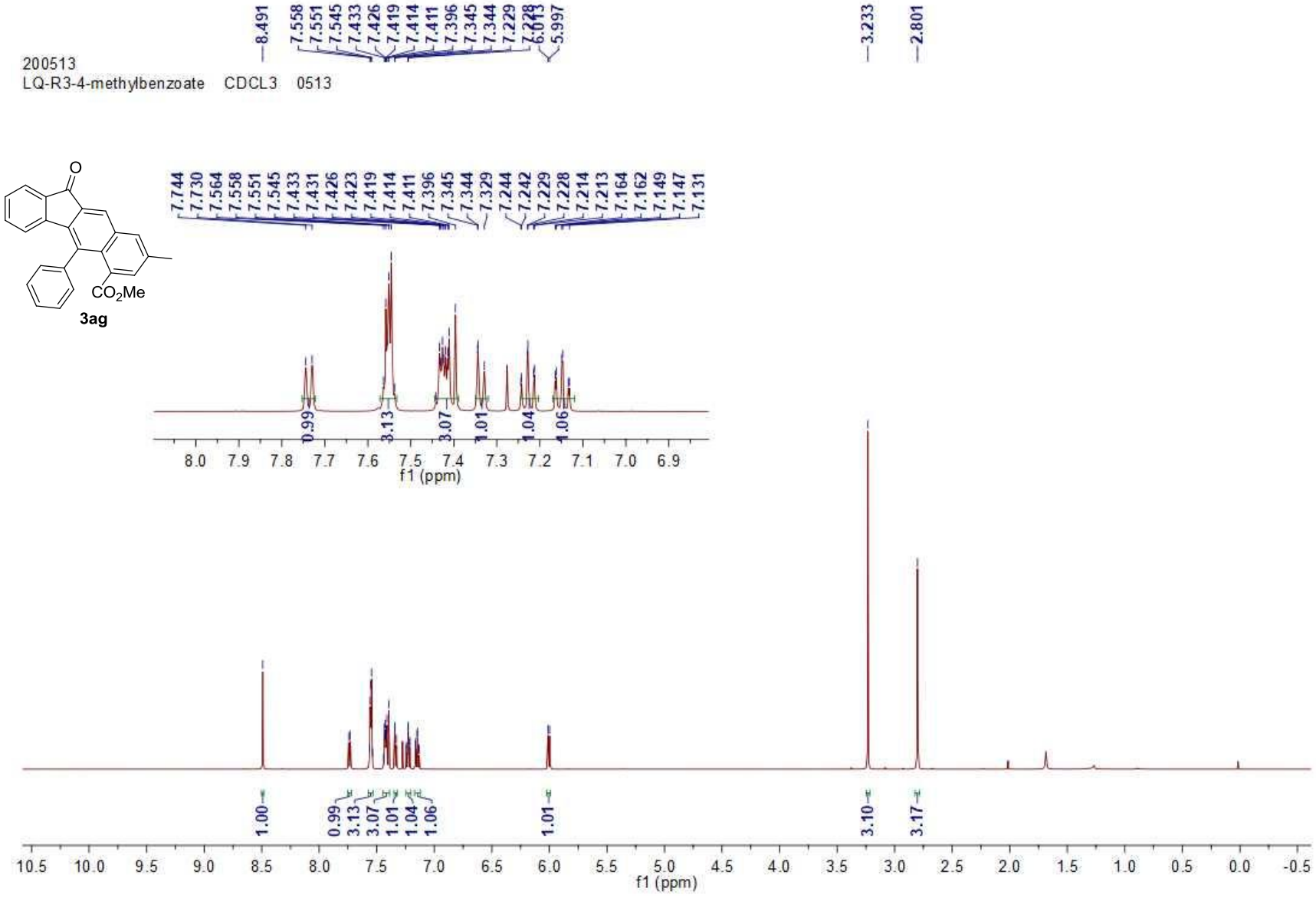
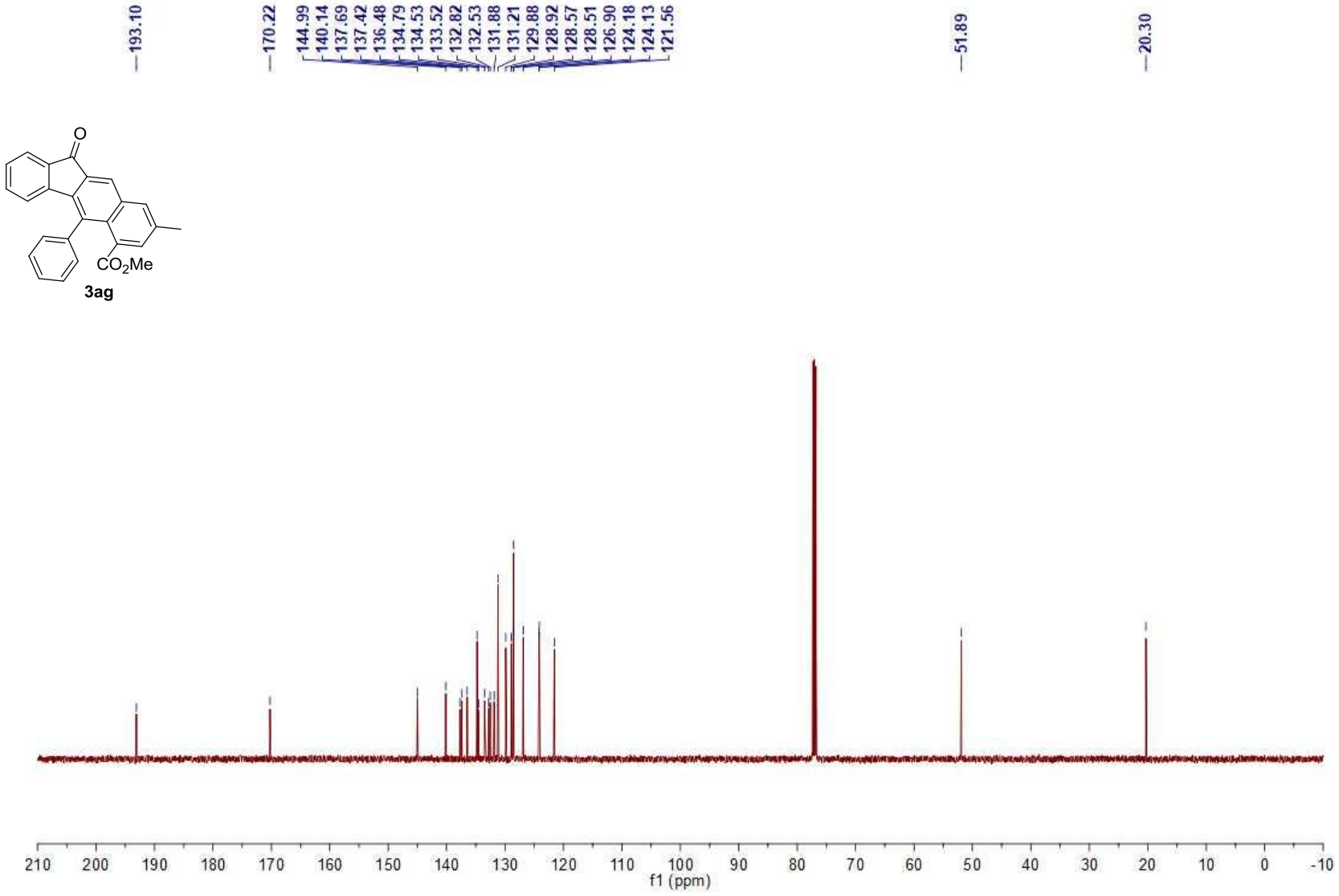
7.621
7.538
7.522
7.504
7.486
7.475
7.453
7.431
7.420
7.206
7.324
6.306
O
3ae
7.724
7.707
7.638
7.621
7.538
7.522
7.504
7.486
7.475
7.453
7.431
7.420
7.409
7.222
7.206
7.186
8E+08
6E+08
4E+08
2E+08
0E+00
1.00
3.01
10.05
2.07
7.9
7.7
7.5
7.3
7.1
f1 (ppm)
1.01
1.00
3.01
10.05
2.07
1.00
10.0
9.5
9.0
8.5
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)

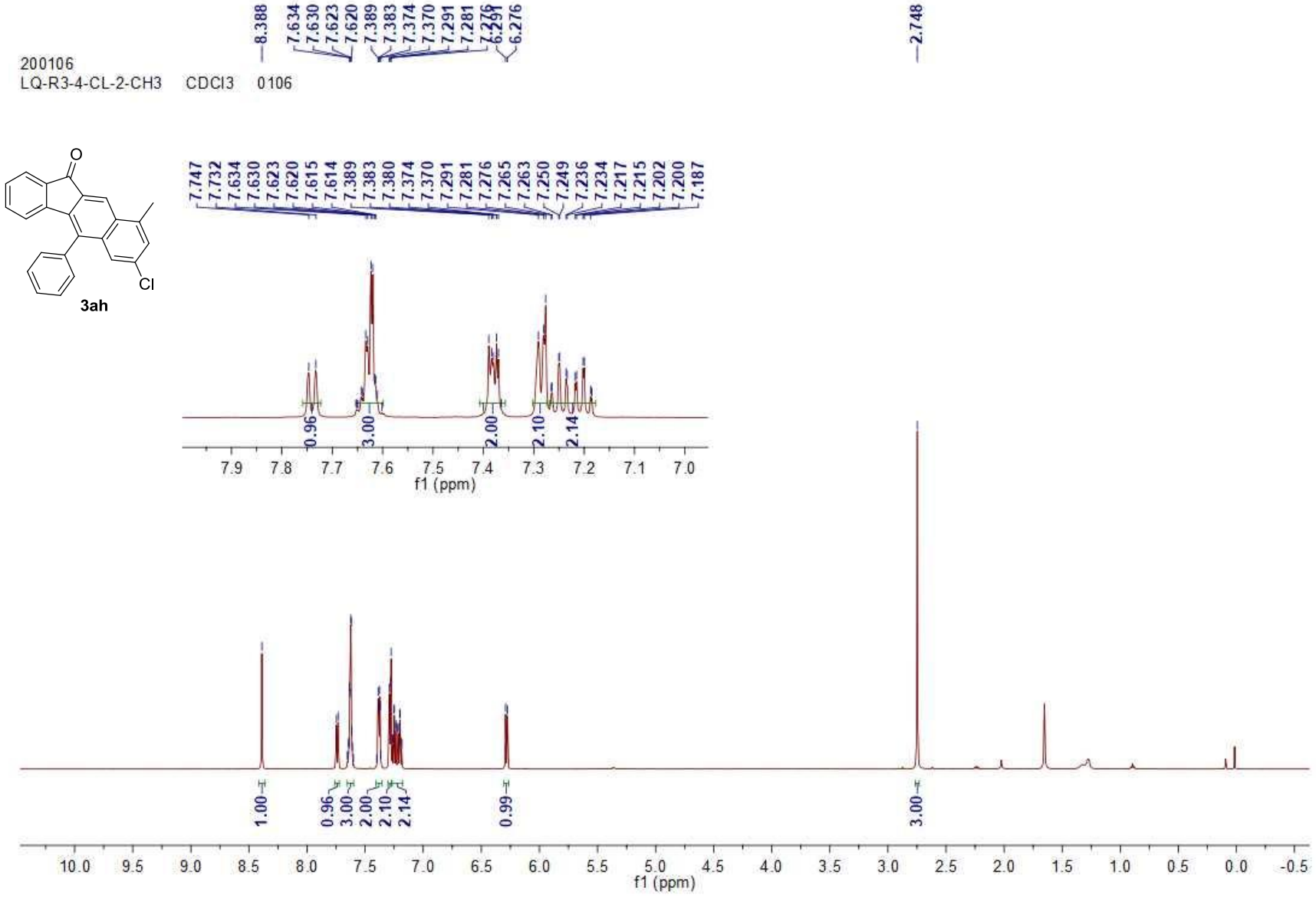

193.22
144.91
143.44
139.95
137.71
137.29
136.58
135.20
134.78
134.64
132.44
131.65
130.00
129.72
129.31
128.65
128.57
128.32
128.25
128.06
127.74
126.64
124.18
123.79
123.62
O
3ae
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

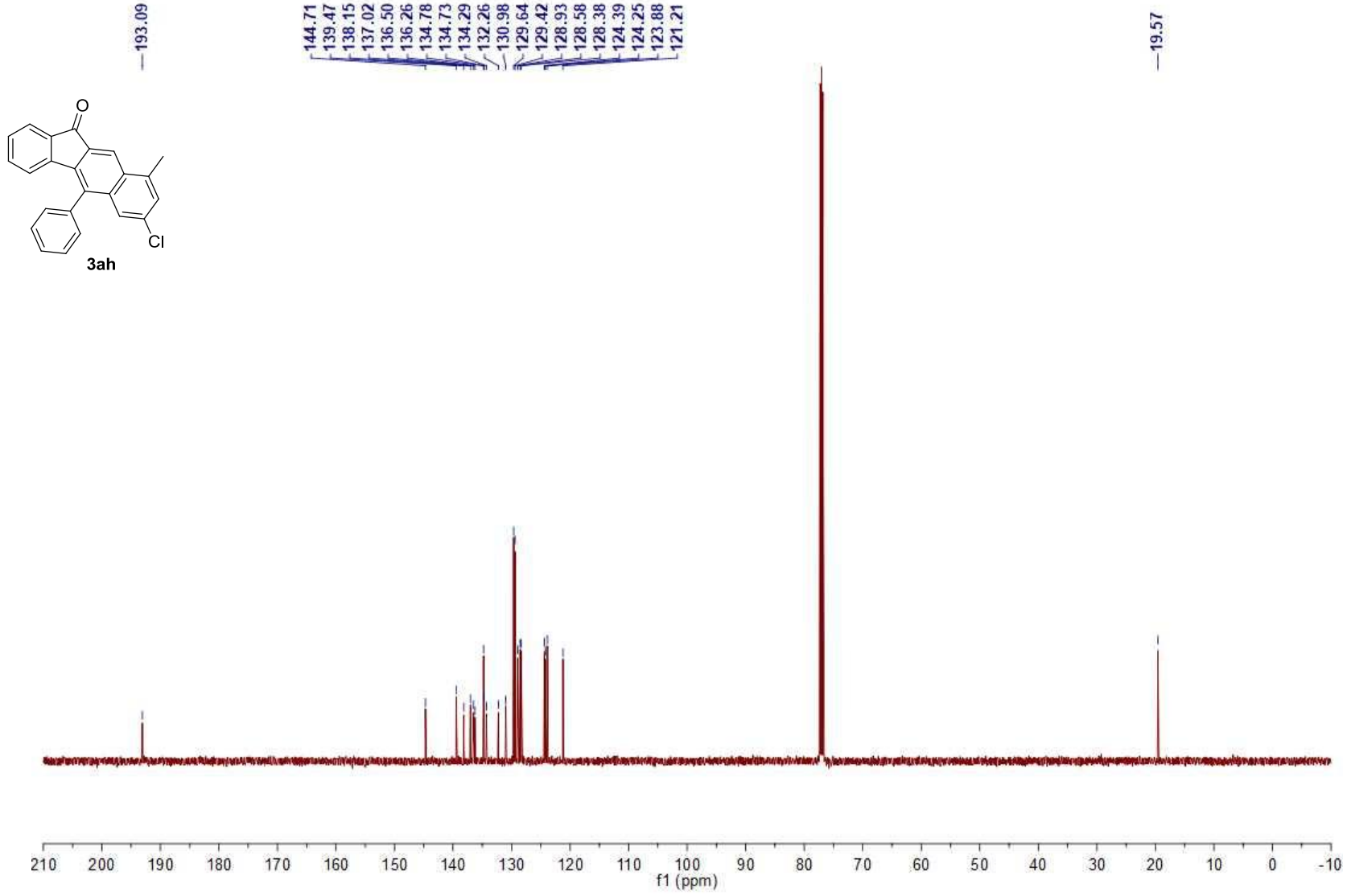

200513
LQ-R3-3,5-dimethyl CDCL3 0513
3af
f1 (ppm)
f1 (ppm)

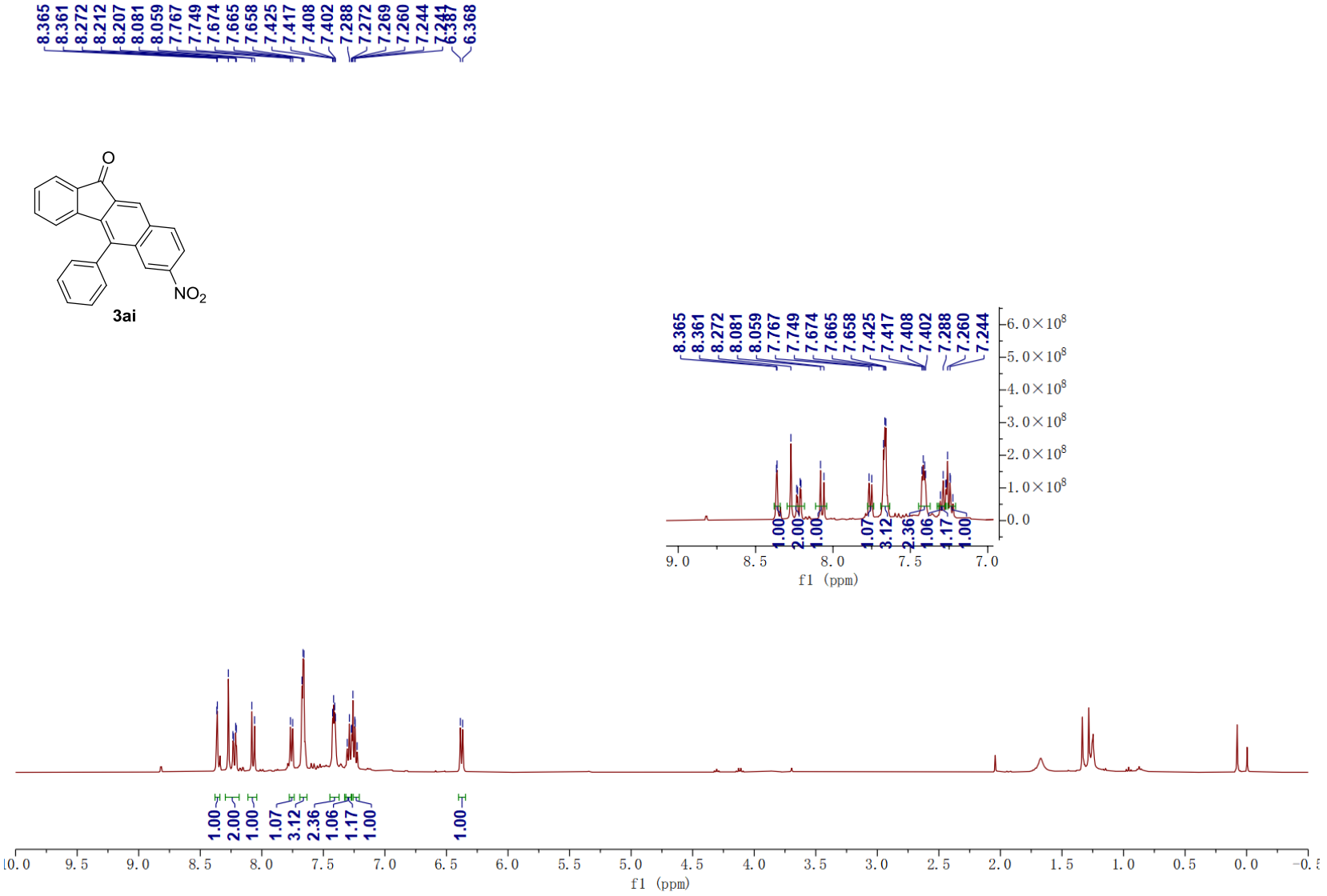

193.22
145.77
141.47
136.90
136.44
136.41
136.12
135.66
135.41
135.19
134.56
132.81
131.61
129.83
129.70
128.80
128.16
128.09
125.82
123.90
123.86
25.03
20.89
O
3af
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

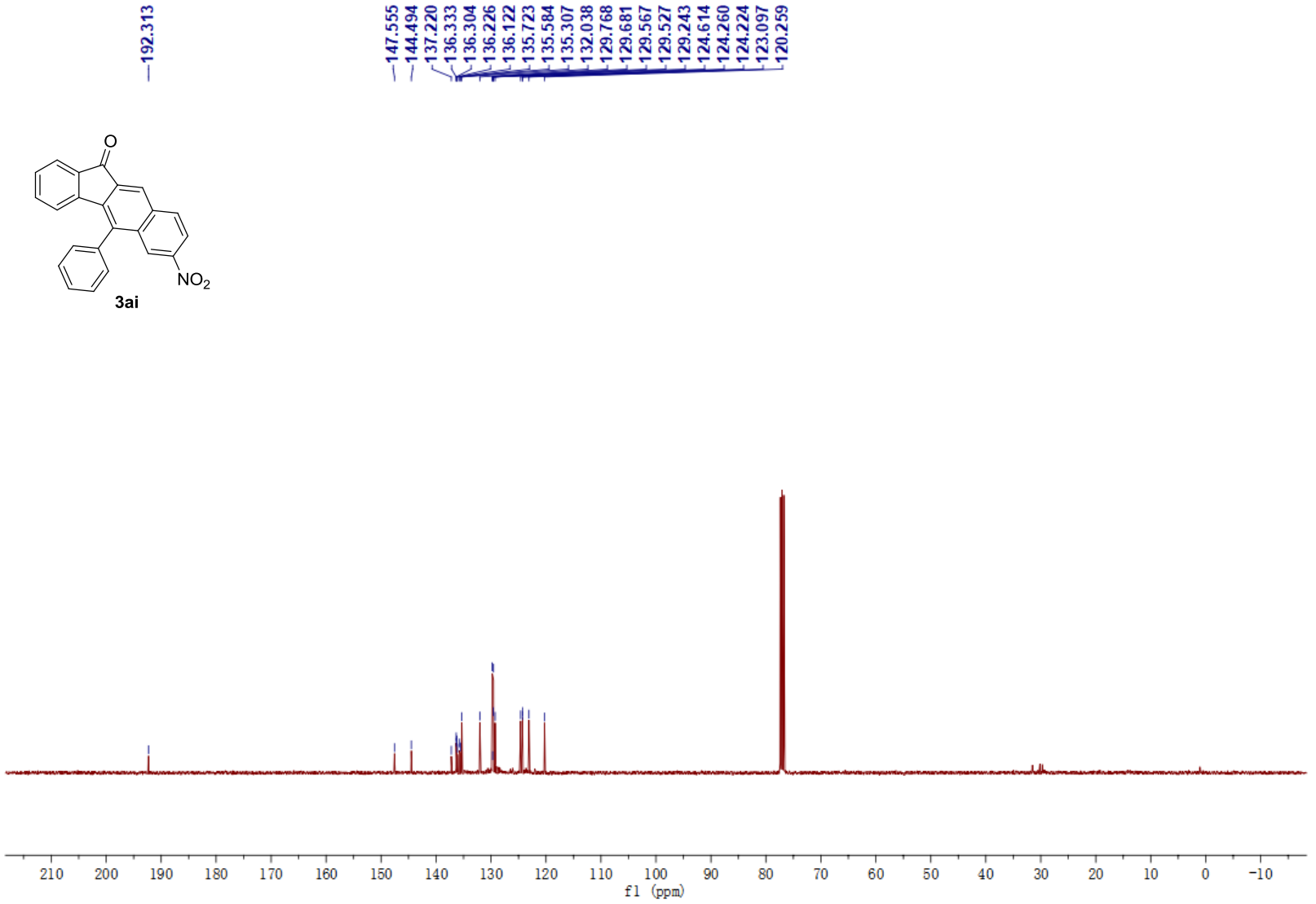

200513
LQ-R3-4-methylbenzoate CDCL3 0513
8.491
7.558
7.551
7.545
7.433
7.426
7.419
7.414
7.411
7.396
7.345
7.344
7.229
6.013
5.997
3.233
2.801
O
CO2Me
3ag
7.744
7.730
7.564
7.558
7.551
7.545
7.433
7.431
7.426
7.423
7.419
7.414
7.411
7.396
7.345
7.344
7.329
7.244
7.242
7.229
7.228
7.214
7.213
7.164
7.162
7.149
7.147
7.131
0.99
3.13
3.07
1.01
1.04
1.06
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
1.00
0.99
3.13
3.07
1.01
1.04
1.06
1.01
3.10
3.17
10.5 10.0 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 -0.5
f1 (ppm)

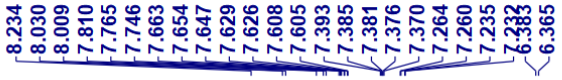

193.10
170.22
144.99
140.14
137.69
137.42
136.48
134.79
134.53
133.52
132.82
132.53
131.88
131.21
129.88
128.92
128.57
128.51
126.90
124.18
124.13
121.56
51.89
20.30
O
CO2Me
3ag
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

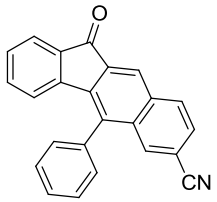

200106
LQ-R3-4-CL-2-CH3 CDCl3 0106
8.388
7.634
7.630
7.623
7.620
7.389
7.383
7.374
7.370
7.291
7.281
6.276
2.748
O
Cl
3ah
7.747
7.732
7.634
7.630
7.623
7.620
7.615
7.614
7.389
7.383
7.380
7.374
7.370
7.291
7.281
7.276
7.265
7.263
7.250
7.249
7.236
7.234
7.217
7.215
7.202
7.200
7.187
0.96
3.00
2.00
2.10
2.14
f1 (ppm)
1.00
0.96
3.00
2.00
2.10
2.14
0.99
3.00
f1 (ppm)


193.09
144.71
139.47
138.15
137.02
136.50
136.26
134.78
134.73
134.29
132.26
130.98
129.64
129.42
128.93
128.58
128.38
124.39
124.25
123.88
121.21
19.57
O
Cl
3ah
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

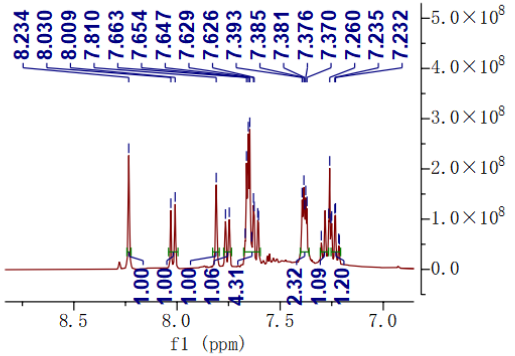

8.365
8.361
8.272
8.212
8.207
8.081
8.059
7.767
7.749
7.674
7.665
7.658
7.425
7.417
7.408
7.402
7.288
7.272
7.269
7.260
7.244
6.387
6.368
O
NO2
3ai
1.00
2.00
1.00
1.07
3.12
2.36
1.06
1.17
1.00
1.00
f1 (ppm)

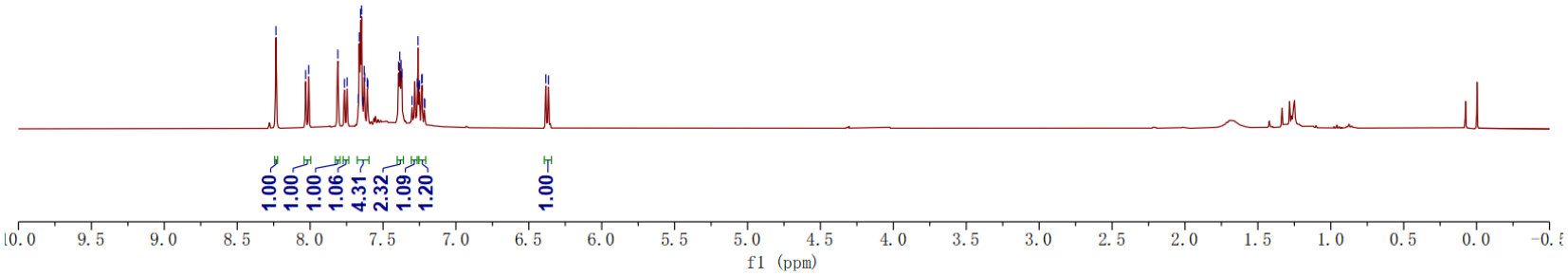

192.313
147.555
144.494
137.220
136.333
136.304
136.226
136.122
135.723
135.584
135.307
132.038
129.768
129.681
129.567
129.527
129.243
124.614
124.260
124.224
123.097
120.259
O
NO2
3ai
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

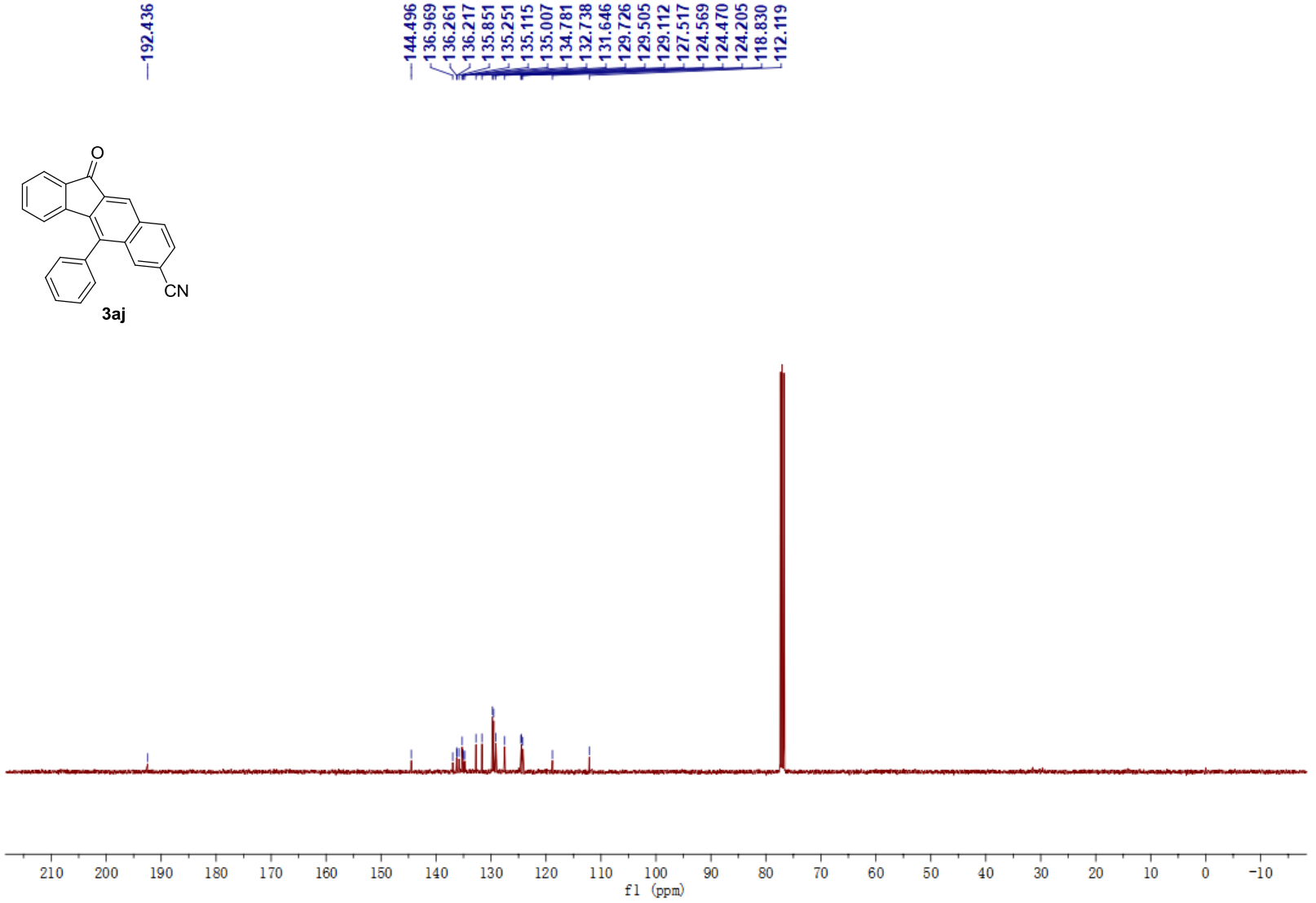

8.234
8.030
8.009
7.810
7.765
7.746
7.663
7.654
7.647
7.629
7.626
7.608
7.605
7.393
7.385
7.381
7.376
7.370
7.264
7.260
7.235
7.233
6.383
6.365


O
CN

3aj


8.234
8.030
8.009
7.810
7.663
7.654
7.647
7.629
7.626
7.393
7.385
7.381
7.376
7.370
7.260
7.235
7.232
5.0×10^8
4.0×10^8
3.0×10^8
2.0×10^8
1.0×10^8
0.0
1.00
1.00
1.00
1.06
4.31
2.32
1.09
1.20
8.5
8.0
7.5
7.0
f1 (ppm)


1.00
1.00
1.00
1.06
4.31
2.32
1.09
1.20
1.00
f1 (ppm)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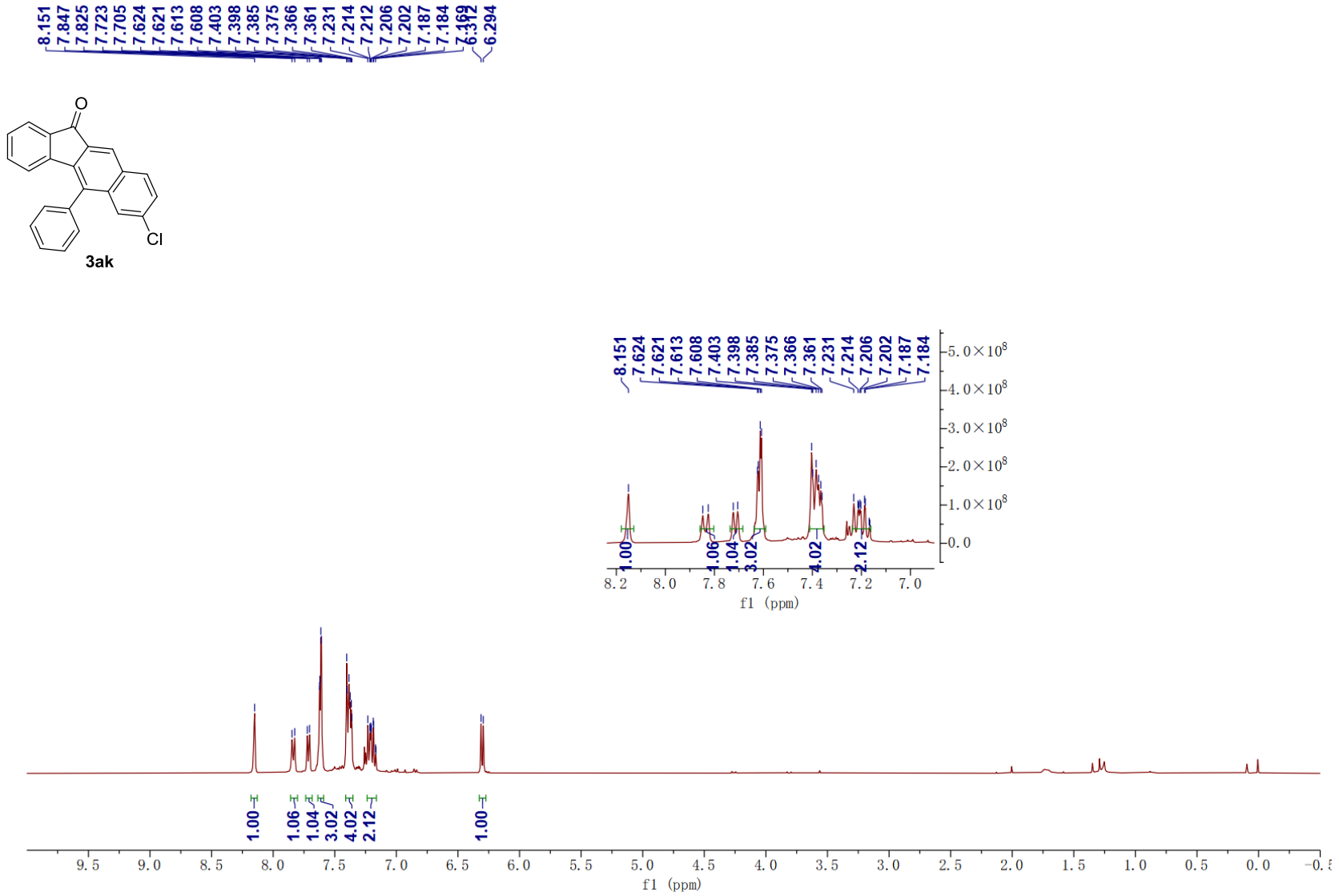
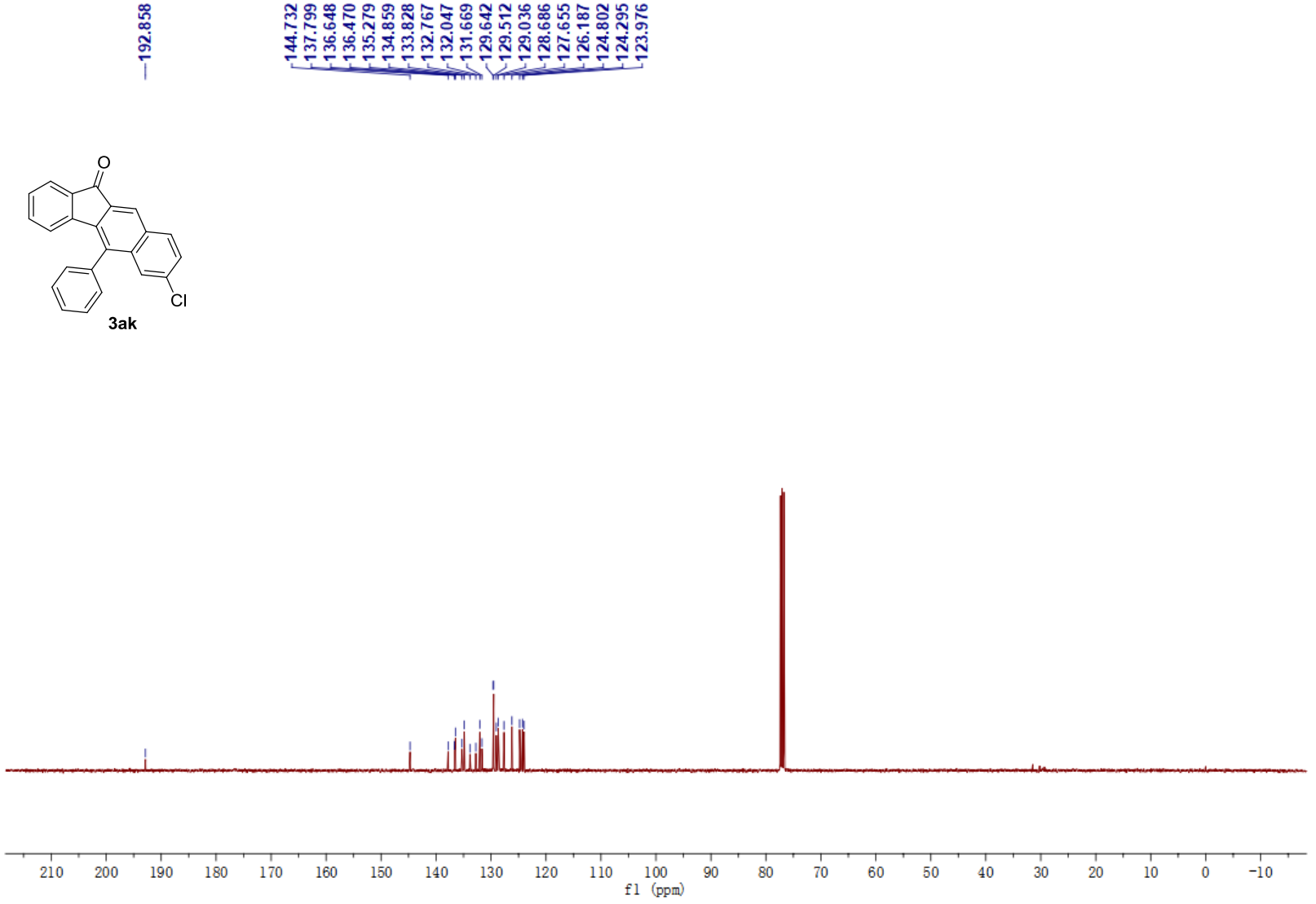
144.496
136.969
136.261
136.217
135.851
135.251
135.115
135.007
134.781
132.738
131.646
129.726
129.505
129.112
127.517
124.569
124.470
124.205
118.830
112.119
O
CN
3aj
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.151
7.847
7.825
7.723
7.705
7.624
7.621
7.613
7.608
7.403
7.398
7.385
7.375
7.366
7.361
7.231
7.214
7.212
7.206
7.202
7.187
7.184
7.169
6.312
6.294
O
Cl
3ak
1.00
1.06
1.04
3.02
4.02
2.12
1.00
f1 (ppm)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137.799
136.648
136.470
135.279
134.859
133.828
132.767
132.047
131.669
129.642
129.512
129.036
128.686
127.655
126.187
124.802
124.295
123.976
O
Cl
3ak
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)