Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

# Supporting information

# Rhenium-Catalyzed Dehydrogenative Olefination of C(sp$^3$)−H Bonds with Hypervalent Iodine(III) Reagents

Haidong Gu and Congyang Wang*

Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Molecular Recognition and Function, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.

Emails: wangcy@iccas.ac.cn

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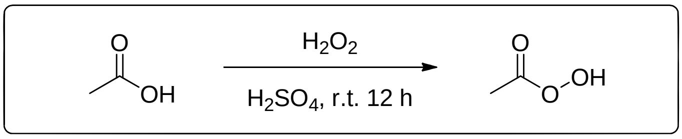
## 1. General Remarks

All chemicals were obtained from commercial sources and were used as received unless otherwise noted. All reactions were carried out in flame-dried reaction vessels with Teflon screw caps under a nitrogen atmosphere by using standard Schlenk techniques. Anhydrous solvents were purified and dried following standard procedures. TLC analysis was performed on pre-coated, glass-backed silica gel plates and visualized with UV light. Column chromatography was performed on silica gel (200-300 mesh) using ethyl acetate (EA)/petroleum ether (PE).

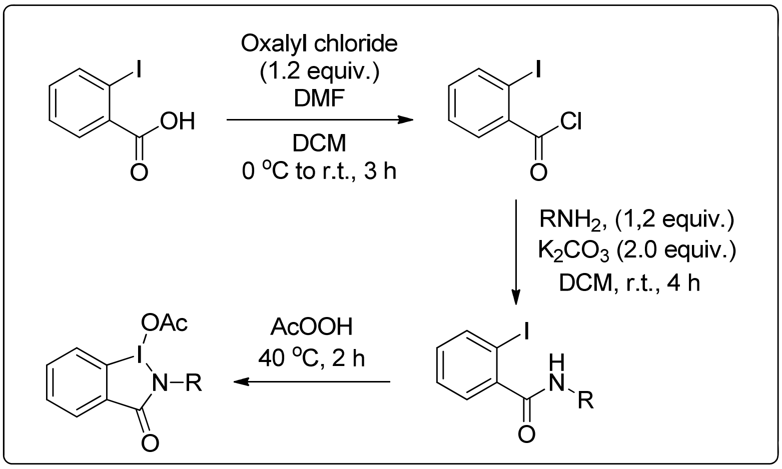
$^{1}$H-NMR and $^{13}$C-NMR Spectra were obtained on a Bruker 300 MHz or 400 MHz NMR spectrometer in the deuterated solvents indicated. $^{19}$F NMR spectra were recorded on a Bruker 500 AV spectrometers. $^{1}$H and $^{13}$C chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak used as an internal reference. The mass spectra (MS) and GC-MS yield were recorded on a SHIMADZU QP-2010SE GC-MS spectrometer. HR-ESI-MS were recorded on a Bruker Apex IV FTMS instrument or a Thermo Scientific Exactive spectrometer. HR-EI-MS spectra were recorded on a GCT-MS Micromass UK spectrometer. HR-MALDI-MS spectra were recorded on a Bruker AUTOFLEX III MALDI-TOF spectrometer.

## 2. Preparation of Substrates

### 2.1 General Procedures for the Synthesis of Hypervalent Iodine(III) Reagents



*Synthesis of peracetic acid* [1]*:* 300 mL of hydrogen peroxide with concentration of 60 percent, 600 mL of acetic acid and 5mL conc. sulfuric acid were mixed for 12 hours at 30°C to synthesize peracetic acid. The prepared solution was used in the next procedures.

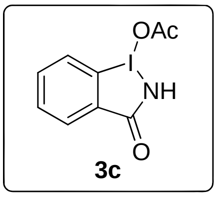


*Synthesis of acid chlorides* [2]*:* 2-iodobenzoic acid (1.0 eq.) was added into a round bottom flask charged with a magnetic stir bar. $CH_2Cl_2$ (0.5 M) was added with a few drops of DMF. The Oxalyl chloride (1.2 eq.) was dropped into the round bottom flask at 0 °C. Then, the reaction mixture was warmed to room temperature for 3 h. The mixture was concentrated in vacuo and the crude product was directly used in the next step.

*Preparation of amides from acid chloride* [3]: $RNH_2$ (1.2 eq.), acid chloride (1.0 eq.), $K_2CO_3$ (2.0 eq.) and $CH_2Cl_2$ (0.5 M) were added into a round bottom flask capped with a septum. The mixture was stirred at room temperature. After 4 h, the crude reaction mixture was extracted with $CH_2Cl_2$, purified by recrystallization (PE: EA=5:1) to yield a white solid.

*Preparation of hypervalent iodine (III) reagents* [4]: The appropriate amide derivative (1 equiv.) was added to a freshly prepared solution of peracetic acid (0.5 M) at room temperature. The reaction mixture was stirred at 40 °C for additional 2 hrs, and then cooled to room temperature. Then the reaction mixture was diluted with 100 mL of cold water. The white precipitate formed after dilution was filtered and washed with water and cold ether and dried in vacuum to afford the pure product.

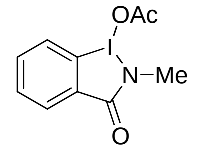
## 2.2 Characterization of Hypervalent Iodine(III) Reagents



**3c**

Following the general procedure: 2-iodobenzamide **6c** (2.47 g, 10 mmol, 1.0 equiv.) was added to a freshly prepared solution of peracetic acid (20 mL, 0.5 M) at room temperature. The reaction mixture was stirred at 40 °C for additional 2 hrs, and then cooled to room temperature. Then the reaction mixture was diluted with 100 mL of cold water. The white precipitate formed after dilution was filtered and washed with water and cold ether and dried in vacuum to afford the pure product **3c**. Yield: 55%. Known compound and the NMR spectral data is in agreement with the literature values. [5]

**$^1$H NMR (400 MHz, DMSO-*d*$_6$)** δ 8.11 (s, 1H), 7.97 (d, *J* = 7.5 Hz, 1H), 7.88 (q, *J* = 8.0, 7.1 Hz, 1H), 7.74 (t, *J* = 7.4 Hz, 1H), 1.98 (s, 3H).



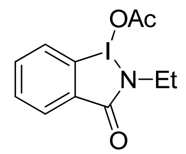
**3d**

Following the general procedure: *N*-methyl-2-iodobenzamide **6d** (2.61 g, 10 mmol, 1.0 equiv.) was added to a freshly prepared solution of peracetic acid (20 mL, 0.5 M) at room temperature. The reaction mixture was stirred at 40 °C for additional 2 hrs, and then cooled to room temperature. Then the reaction mixture was diluted with 100 ml of cold water. The white precipitate formed after dilution was filtered and washed with water and cold ether and dried in vacuum to afford the pure product **3d**. Yield: 60%. Known compound and the spectral data are in agreement with the literature values. [6]

**$^1$H NMR (300 MHz, CDCl$_3$)** δ 8.25 – 8.12 (m, 2H), 7.84 – 7.74 (m, 1H), 7.68 (t, *J* = 7.3 Hz, 1H), 3.23 (s, 3H), 2.16 (s, 3H).

**$^{13}$C NMR (75 MHz, CDCl$_3$)** δ 177.9, 167.0, 134.7, 132.2, 131.6, 130.9, 130.2, 116.7,

29.3, 21.9.


**3e**

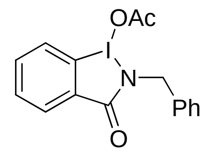
Following the general procedure: *N*-ethyl-2-iodobenzamide **6e** (2.75 g, 10 mmol, 1.0 equiv.) was added to a freshly prepared solution of peracetic acid (20 mL, 0.5 M) at room temperature. The reaction mixture was stirred at 40 °C for additional 2 hrs, and then cooled to room temperature. Then the reaction mixture was diluted with 100 mL of cold water. The white precipitate formed after dilution was filtered and washed with water and cold ether and dried in vacuum to afford the pure product **3e**. Yield: 57%.

**m.p.:** 156-158 ºC.

**$^1$H NMR (300 MHz, CDCl$_3$)** δ 8.18 (d, *J* = 8.0 Hz, 2H), 7.83 – 7.73 (m, 1H), 7.68 (t, *J* = 7.4 Hz, 1H), 3.70 (q, *J* = 7.2 Hz, 2H), 2.16 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H).

**$^{13}$C NMR (75 MHz, CDCl$_3$)** δ 177.9, 166.3, 134.5, 132.7, 131.6, 130.9, 130.2, 116.7, 38.1, 21.9, 16.1.

**HRMS (MALDI-MS):** calculated $C_{11}H_{12}IKNO_3^+$ ([M+K]$^+$): 371.94989, found: 371.94935.


**3f**

Following the general procedure: *N*-benzyl-2-iodobenzamide **6f** (3.37 g, 10 mmol, 1.0 equiv.) was added to a freshly prepared solution of peracetic acid (20 mL, 0.5 M) at room temperature. The reaction mixture was stirred at 40 °C for additional 2 hrs, and then cooled to room temperature. Then the reaction mixture was diluted with 100 mL of cold water. The white precipitate formed after dilution was filtered and washed with water and cold ether and dried in vacuum to afford the pure product **3f**. Yield: 54%.

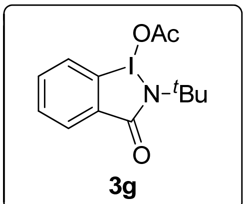
**m.p.:** 154 ºC.

**$^1$H NMR (300 MHz, CDCl$_3$)** δ 8.23 (dd, *J* = 7.4, 1.6 Hz, 1H), 8.11 (d, *J* = 8.2 Hz, 1H), 7.80 – 7.65 (m, 2H), 7.46 – 7.36 (m, 5H), 4.82 (s, 2H), 2.07 (s, 3H).

**$^{13}$C NMR (75 MHz, CDCl$_3$)** δ 177.7, 166.1, 137.8, 134.5, 133.2, 131.7, 130.9, 130.2,

129.5, 128.8, 128.7, 117.3, 47.8, 21.8.

**HRMS (MALDI-MS):** calculated $C_{16}H_{14}IKNO_3^+$ ($[M+K]^+$): 433.96554, found: 433.96500.



**3g**

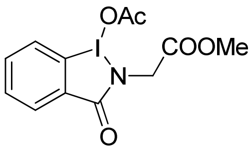
Following the general procedure: *N*-(*tert*-butyl)-2-iodobenzamide **6g** (3.03 g, 10 mmol, 1.0 equiv.) was added to a freshly prepared solution of peracetic acid (20 mL, 0.5 M) at room temperature. The reaction mixture was stirred at 40 °C for additional 2 hrs, and then cooled to room temperature. Then the reaction mixture was diluted with 100 mL of cold water. The white precipitate formed after dilution was filtered and washed with water and cold ether and dried in vacuum to afford the pure product **6g**. Yield: 55%.

**m.p.:** 108-109 ºC.

**$^1$H NMR (300 MHz, CDCl$_3$)** δ 8.13 (t, *J* = 7.0 Hz, 2H), 7.80 – 7.71 (m, 1H), 7.66 (t, *J* = 7.4 Hz, 1H), 2.15 (s, 3H), 1.66 (s, 9H).

**$^{13}$C NMR (75 MHz, CDCl$_3$)** δ 177.9, 165.7, 135.2, 134.2, 131.5, 130.8, 129.7, 114.7, 57.8, 30.20, 21.9.

**HRMS (MALDI-MS):** calculated $C_{13}H_{16}IKNO_3^+$ ($[M+K]^+$): 399.98119, found: 399.98065.



**3h**

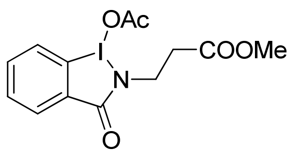
Following the general procedure: methyl 2-(2-iodobenzamido)-acetate **6h** (3.19 g, 10 mmol, 1.0 equiv.) was added to a freshly prepared solution of peracetic acid (20 mL, 0.5 M) at room temperature. The reaction mixture was stirred at 40 °C for additional 2 hrs, and then cooled to room temperature. Then the reaction mixture was diluted with 100 mL of cold water. The white precipitate formed after dilution was filtered and washed with water and cold ether and dried in vacuum to afford the pure product **3h**. Yield: 61%.

**m.p.:** 174-175 ºC.

**$^1$H NMR (300 MHz, CDCl$_3$)** δ 8.22 (dd, *J* = 7.5, 1.5 Hz, 2H), 7.85 – 7.73 (m, 1H), 7.66 (t, *J* = 7.4 Hz, 1H), 4.57 (s, 2H), 3.88 (s, 3H), 2.17 (s, 3H).

**$^{13}$C NMR (75 MHz, CDCl$_3$)** δ 177.7, 172.1, 167.7, 134.5, 132.3, 131.0, 130.6, 130.1, 118.0, 53.4, 46.3, 21.7.

**HRMS (MALDI-MS):** calculated $C_{12}H_{12}IKNO_5^+$ ([M+K]$^+$): 415.93972, found: 415.93918.



**3i**

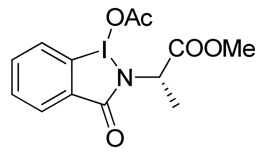
Following the general procedure: methyl 3-(2-iodobenzamido)-propanoate **6i** (3.33 g, 10 mmol, 1.0 equiv.) was added to a freshly prepared solution of peracetic acid (20 mL, 0.5 M) at room temperature. The reaction mixture was stirred at 40 °C for additional 2 hrs, and then cooled to room temperature. Then the reaction mixture was diluted with 100 mL of cold water. The white precipitate formed after dilution was filtered and washed with water and cold ether and dried in vacuum to afford the pure product **3i**. Yield: 61%.

**m.p.:** 141-143 ºC.

**$^{1}$H NMR (300 MHz, CDCl$_3$)** δ 8.16 (ddd, *J* = 14.5, 7.9, 1.1 Hz, 2H), 7.83 – 7.73 (m, 1H), 7.66 (td, *J* = 7.4, 0.9 Hz, 1H), 3.96 – 3.86 (m, 2H), 3.77 (s, 3H), 2.80 – 2.69 (m, 2H), 2.17 (s, 3H).

**$^{13}$C NMR (75 MHz, CDCl$_3$)** δ 177.5, 173.7, 167.2, 134.6, 132.3, 131.3, 130.6, 129.9, 117.4, 52.4, 38.5, 34.4, 21.8.

**HRMS (MALDI-MS):** calculated $C_{13}H_{14}IKNO_5^+$ ([M+K]$^+$): 429.95537, found: 429.95483.



**3j**

Following the general procedure: methyl 2-(2-iodobenzamido)-propanoate **6j** (3.33 g, 10 mmol, 1.0 equiv.) was added to a freshly prepared solution of peracetic acid (20 mL, 0.5 M) at room temperature. The reaction mixture was stirred at 40 °C for additional 2 hrs, and then cooled to room temperature. Then the reaction mixture was diluted with 100 mL of cold water. The white precipitate formed after dilution was filtered and washed with water and cold ether and dried in vacuum to afford the pure product **6j**. Yield: 65%. Known compound and the NMR spectral data is in agreement with the literature value. [4]

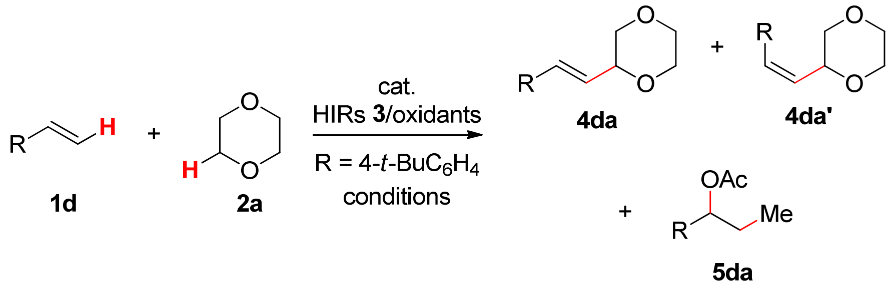
**$^1$H NMR (300 MHz, CDCl$_3$)** δ 8.19 (d, *J* = 8.0 Hz, 2H), 7.84 – 7.70 (m, 1H), 7.65 (t, *J* = 7.4 Hz, 1H), 5.11 (q, *J* = 6.8 Hz, 1H), 3.88 (s, 3H), 2.18 (s, 3H), 1.52 (d, *J* = 7.0 Hz, 3H).

**$^{13}$C NMR (75 MHz, CDCl$_3$)** δ 177.5, 175.2, 166.7, 134.2, 132.6, 130.8, 130.4, 129.9, 117.6, 53.4, 53.1, 21.6, 19.7.

# 3. Re-Catalyzed Dehydrogenative Olefination of C(sp$^3$)-H Bonds with HIRs

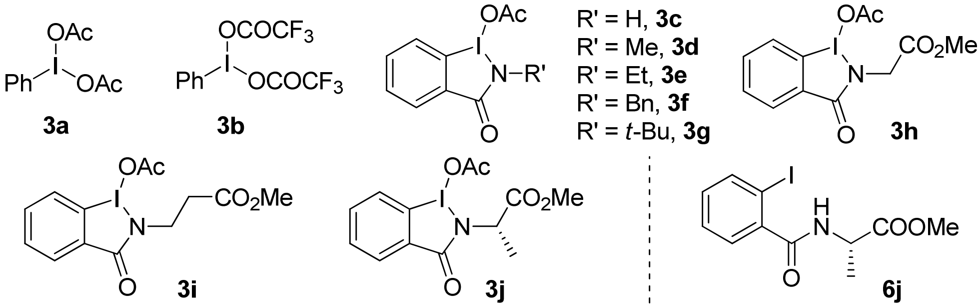
## 3.1 Optimization of Reaction Parameters

**Table S1.** Survey of the reaction conditions[a]



| Entry | Cat. (mol %) | Oxidants | Conditions | Yield(%)[b] | | |
|---|---|---|---|---|---|---|
| | | | | **4da** | **4da'** | **5da** |
| 1 | $Re_2(CO)_{10}$ (2.5) | **3a** | 120 ℃, 3 h | 12 | 0 | 19 |
| 2[c] | $Re_2(CO)_{10}$ (2.5) | **3b** | 120 ℃, 3 h | 0 | 0 | 0 |
| 3 | $Re_2(CO)_{10}$ (2.5) | **3c** | 120 ℃, 3 h | 0 | 0 | 0 |
| 4 | $Re_2(CO)_{10}$ (2.5) | **3d** | 120 ℃, 3 h | 15 | 0 | 0 |
| 5 | $Re_2(CO)_{10}$ (2.5) | **3e** | 120 ℃, 3 h | 53 | 0 | 0 |
| 6 | $Re_2(CO)_{10}$ (2.5) | **3f** | 120 ℃, 3 h | 46 | 0 | 0 |
| 7 | $Re_2(CO)_{10}$ (2.5) | **3g** | 120 ℃, 3 h | 55 | 0 | 0 |
| 8 | $Re_2(CO)_{10}$ (2.5) | **3h** | 120 ℃, 3 h | 48 | 0 | 0 |
| 9 | $Re_2(CO)_{10}$ (2.5) | **3i** | 120 ℃, 3 h | 64 | 0 | 0 |
| 10 | $Re_2(CO)_{10}$ (2.5) | **3j** | 120 ℃, 3 h | 73 | 0 | 0 |
| 11 | $Re_2(CO)_{10}$ (2.5) | TBHP | 120 ℃, 3 h | 15 | 0 | 0 |
| 12 | $Re_2(CO)_{10}$ (2.5) | $(^tBuO)_2$ | 120 ℃, 3 h | 5 | 0 | 0 |
| 13 | $Re_2(CO)_{10}$ (2.5) | *m*-CPBA | 120 ℃, 3 h | 6 | 0 | 0 |
| 14 | $Re_2(CO)_{10}$ (2.5) | oxone | 120 ℃, 3 h | 0 | 0 | 0 |
| 15 | $Re_2(CO)_{10}$ (2.5) | $NaIO_4$ | 120 ℃, 3 h | 0 | 0 | 0 |
| 16 | $Re_2(CO)_{10}$ (2.5) | $(PhCOO)_2$ | 120 ℃, 3 h | 30 | 0 | 0 |
| 17 | $Re_2(CO)_{10}$ (2.5) | BQ | 120 ℃, 3 h | 0 | 0 | 0 |
| 18 | -[d] | **3j** | 120 ℃, 3 h | 24 | 0 | 0 |
| 19 | CuBr (5) | **3j** | 120 ℃, 3 h | 14 | 0 | 0 |
| 20 | $CuBr_2$ (5) | **3j** | 120 ℃, 3 h | 7 | 0 | 0 |
| 21 | $FeCl_2$ (5) | **3j** | 120 ℃, 3 h | 8 | 0 | 0 |

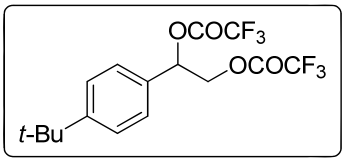
| | | | | | | |
|---|---|---|---|---|---|---|
| 22 | $FeCl_3$ (5) | **3j** | 120 ℃, 3 h | 9 | 0 | 0 |
| 23 | $ZnCl_2$ (5) | **3j** | 120 ℃, 3 h | 0 | 0 | 0 |
| 24 | $Mn_2(CO)_{10}$ (5) | **3j** | 120 ℃, 3 h | 10 | 0 | 0 |
| 25 | $Mn(CO)_5Br$ (5) | **3j** | 120 ℃, 3 h | 8 | 0 | 0 |
| 26 | $Mn(OAc)_2$ (5) | **3j** | 120 ℃, 3 h | 0 | 0 | 0 |
| 27 | $Pd(OAc)_2$ (5) | **3j** | 120 ℃, 3 h | 0 | 0 | 0 |
| 28 | AgOAc (5) | **3j** | 120 ℃, 3 h | 0 | 0 | 0 |
| 29 | $Yb(OTf)_3$ (5) | **3j** | 120 ℃, 3 h | 22 | 0 | 0 |
| 30 | $In(OTf)_3$ (5) | **3j** | 120 ℃, 3 h | 24 | 0 | 0 |
| 31 | $Sc(OTf)_3$ (5) | **3j** | 120 ℃, 3 h | 19 | 0 | 0 |
| 32 | $Re(CO)_5Cl$ (5) | **3j** | 120 ℃, 3 h | 48 | 0 | 0 |
| 33 | $Re(CO)_5Br$ (5) | **3j** | 120 ℃, 3 h | 18 | 0 | 0 |
| 34 | $Re_2(CO)_{10}$ (1) | **3j** | 120 ℃, 3 h | 63 | 0 | 0 |
| 35 | $Re_2(CO)_{10}$ (2.5) | **3j** | 120 ℃, 2 h | 70 | 0 | 0 |
| 36 | $Re_2(CO)_{10}$ (2.5) | **3j** | 120 ℃, 4 h | 68 | 0 | 0 |
| 37 | $Re_2(CO)_{10}$ (2.5) | **3j** | 120 ℃, 6 h | 64 | 0 | 0 |
| 38 | $Re_2(CO)_{10}$ (2.5) | **3j** | 100 ℃, 3 h | 39 | 0 | 0 |
| 39 | $Re_2(CO)_{10}$ (2.5) | **3j** | 140 ℃, 3 h | 59 | 0 | 0 |
| 40[e] | $Re_2(CO)_{10}$ (2.5) | **3j** | 120 ℃, 3 h | 75 | 0 | 0 |
| 41[f] | $Re_2(CO)_{10}$ (2.5) | **3j** | 120 ℃, 4 h | 80 | 0 | 0 |
| **42**[g] | **$Re_2(CO)_{10}$ (2.5)** | **3j** | **120 ℃, 4 h** | **84**<br>**(66)**[h] | **0** | **0** |



[a] All reactions were carried out on 0.2 mmol scale in 1,4-dioxane (0.1 M) for 3 h unless otherwise noted. [b] The yields was determined by GC-MS in reaction mixture and use mesitylene (0.1 mmol) as internal standard. [c] Ditrifluoroacetoxylation product was formed in 65% isolated yield.[7] [d] No catalyst. [e] **3j** (0.6 mmol). [f] **3j** (0.6 mmol), 1,4-dioxane (0.067M). [g] **3j** (0.8 mmol), 1,4-dioxane (0.05 M). [h] Isolated yield of the

pure product **4da** on 1.0 mmol scale, 2-iodobenzamide **6j** was isolated in 96 % yield.

Ditrifluoroacetoxylation product:



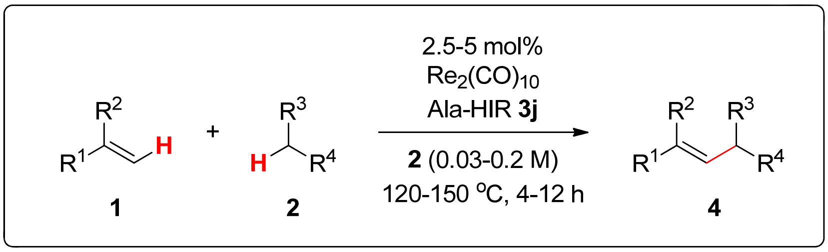
**$^1$H NMR (300 MHz, CDCl$_3$)** δ 7.46 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 6.22 (dd, *J* = 9.2, 3.2 Hz, 1H), 4.72 (dd, *J* = 12.2, 9.1 Hz, 1H), 4.58 (dd, *J* = 12.2, 3.2 Hz, 1H), 1.32 (s, 9H).

**$^{13}$C NMR (75 MHz, CDCl$_3$)** δ 157.2, 156.6, 153.7, 129.6, 127.8, 126.7, 126.4, 114.5, 76.4, 68.0, 35.0, 31.3.

**$^{19}$F NMR (471 MHz, CDCl$_3$)** δ -74.97, -75.10.

**HRMS (EI-MS):** calculated $C_{16}H_{16}F_6O_4$ ([M]): 386.0953, found: 386.0954.

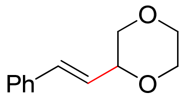
## 3.2 General Procedures for Dehydrogenative Olefination Reactions



$Re_2(CO)_{10}$ (16.4 mg, 0.025 mmol, 2.5 mol%) was added into an oven-dried reaction vessel with Teflon screw cap under nitrogen atmosphere. Then, hypervalent iodine (III) reagents **3j** (1.56 g, 4.0 mmol, 4.0 eq.), **2** (0.05 M) and olefin **1** (1 mmol, 1.0 eq.) were subjected in sequence to the reaction tube. The reaction mixture was stirred in an oil bath at 120 °C for 4 h. Then the reaction mixture was cooled down to room temperature, diluted with $CH_2Cl_2$ (5 mL), and filtered through a short pad of silica, which was then washed with $CH_2Cl_2$ (30 mL). After the removal of the volatiles in vacuo, the crude mixture was pre-adsorbed on silica gel and purified by flash column chromatography (EA : PE = 1:50~1:10) to obtain the product **4**. In addition, methyl 2-(2-iodobenzamido) propanoate **6j** can be recovered in approximately quantitative yield (PE: EA=5:1).

## 3.3 Characterization of Products:

### (*E*)-2-styryl-1,4-dioxane (4aa) [8]



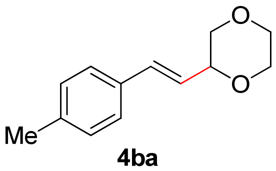
**4aa**

Following the general procedure with slight modification: $Re_2(CO)_{10}$ (32.8 mg, 0.05 mmol, 5 mol%) was added into an oven-dried reaction vessel with Teflon screw cap under nitrogen atmosphere. Then, hypervalent iodine(III) reagent **3j** (1.56 g, 4.0 mmol, 4.0 eq.), 1,4-dioxane (30 mL, 0.033 M) and styrene **1a** (104 mg, 1 mmol, 1.0 eq.) were subjected in sequence to the reaction tube. The reaction mixture was stirred in an oil bath at 150 °C for 4 h. Then the reaction mixture was cooled down to room temperature, diluted with $CH_2Cl_2$ (5 mL), and filtered through a short pad of silica, which was then washed with $CH_2Cl_2$ (30 mL). After the removal of the volatiles in vacuo, the crude mixture was pre-adsorbed on silica gel and purified by flash column chromatography. The product **4aa** was obtained in 72 % isolated yield as colorless oil.

**$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.38 – 7.23 (m, 5H), 6.68 (d, *J* = 16.1 Hz, 1H), 6.07 (dd, *J* = 16.1, 6.1 Hz, 1H), 4.29 – 4.18 (m, 1H), 3.91 – 3.58 (m, 5H), 3.41 (t, *J* = 6.0 Hz, 1H).

**$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 136.5, 132.7, 128.7, 128.0, 126.6, 125.3, 76.2, 71.1, 66.7, 66.4.

### (*E*)-2-(4-methylstyryl)-1,4-dioxane (4ba)



**4ba**

Following the general procedure: $Re_2(CO)_{10}$ (16.4 mg, 0.025 mmol, 2.5 mol%) was added into an oven-dried reaction vessel with Teflon screw cap under nitrogen atmosphere. Then, hypervalent iodine(III) reagent **3j** (1.56 g, 4.0 mmol, 4.0 eq.), 1,4-dioxane (20 mL, 0.05 M) and 1-methyl-4-vinylbenzene **1b** (118 mg, 1 mmol, 1.0 eq.) were subjected in sequence to the reaction tube. The reaction mixture was stirred in an oil bath at 120 °C for 4 h. Then the reaction mixture was cooled down to room temperature, diluted with $CH_2Cl_2$ (5 mL), and filtered through a short pad of silica, which was then washed with $CH_2Cl_2$ (30 mL). After the removal of the volatiles in vacuo, the crude mixture was pre-adsorbed on silica gel and purified by flash column chromatography. The product **4ba** was obtained in 66 % isolated yield as white solid.

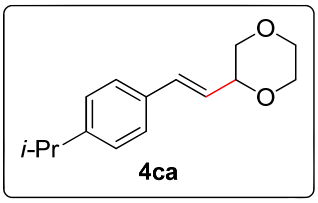
**m.p.:** 65-66 ºC.

**$^1$H NMR (300 MHz, CDCl$_3$)** δ 7.26 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.64 (d, *J* = 16.1 Hz, 1H), 6.02 (dd, *J* = 16.1, 6.3 Hz, 1H), 4.28 – 4.16 (m, 1H), 3.90 – 3.58 (m, 5H), 3.41 (t, *J* = 6.0 Hz, 1H), 2.32 (s, 3H).

**$^{13}$C NMR (75 MHz, CDCl$_3$)** δ 137.9, 133.7, 132.7, 129.4, 126.5, 124.1, 76.3, 71.1, 66.7, 66.4, 21.3.

**HRMS (ESI-MS):** calculated $C_{13}H_{17}O_2^+$ ([M+H]$^+$): 205.12231, found: 205.12252.

**(*E*)-2-(4-isopropylstyryl)-1,4-dioxane (4ca)**



4ca

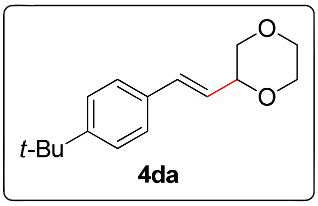
Following the general procedure: $Re_2(CO)_{10}$ (16.4 mg, 0.025 mmol, 2.5 mol%) was added into an oven-dried reaction vessel with Teflon screw cap under nitrogen atmosphere. Then, hypervalent iodine(III) reagent **3j** (1.56 g, 4.0 mmol, 4.0 eq.), 1,4-dioxane (20 mL, 0.05 M), and 1-isopropyl-4-vinylbenzene **1c** (146 mg, 1 mmol, 1.0 eq.) were subjected in sequence to the reaction tube. The reaction mixture was stirred in an oil bath at 120 °C for 4 h. Then the reaction mixture was cooled down to room temperature, diluted with $CH_2Cl_2$ (5 mL), and filtered through a short pad of silica, which was then washed with $CH_2Cl_2$ (30 mL). After the removal of the volatiles in vacuo, the crude mixture was pre-adsorbed on silica gel and purified by flash column chromatography. The product **4ca** was obtained in 56 % isolated yield as colorless oil.

**$^1$H NMR (300 MHz, CDCl$_3$)** δ 7.30 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 6.65 (d, *J* = 15.6 Hz, 1H), 6.03 (dd, *J* = 16.1, 6.3 Hz, 1H), 4.29 – 4.17 (m, 1H), 3.90 – 3.59 (m, 5H), 3.40 (t, *J* = 4.5 Hz, 1H), 2.88 (p, *J* = 6.9 Hz, 1H), 1.23 (d, *J* = 6.9 Hz, 6H).

**$^{13}$C NMR (75 MHz, CDCl$_3$)** δ 148.9, 134.2, 132.7, 126.8, 126.6, 124.4, 76.3, 71.1, 66.7, 66.4, 34.0, 24.0.

**HRMS (ESI-MS):** calculated $C_{15}H_{21}O_2^+$ ($[M+H]^+$): 233.15361, found: 233.15387.

### (*E*)-2-(4-(*tert*-butyl)styryl)-1,4-dioxane (4da)



**4da**

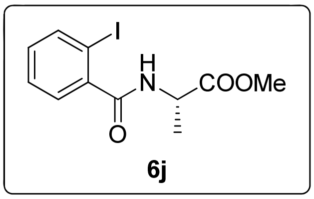
Following the general procedure: $Re_2(CO)_{10}$ (16.4 mg, 0.025 mmol, 2.5 mol%) was added into an oven-dried reaction vessel with Teflon screw cap under nitrogen atmosphere. Then, hypervalent iodine(III) reagent **3j** (1.56 g, 4.0 mmol, 4.0 eq.), 1,-dioxane (20 mL, 0.05 M) and 1-(*tert*-butyl)-4-vinylbenzene **1d** (160 mg, 1 mmol, 1.0 eq.) were subjected in sequence to the reaction tube. The reaction mixture was stirred in an oil bath at 120 °C for 4 h. Then the reaction mixture was cooled down to room temperature, diluted with $CH_2Cl_2$ (5 mL), and filtered through a short pad of silica, which was then washed with $CH_2Cl_2$ (30 mL). After the removal of the volatiles in vacuo, the crude mixture was pre-adsorbed on silica gel and purified by flash column chromatography. The product **4da** was obtained in 66 % isolated yield as colorless oil. Meanwhile, methyl 2-(2-iodobenzamido)propanoate **6j** was obtained in 96% isolated yield. In addition, the product **4da** is a racemic mixture detected by a chiral HPLC spectrometer.

**$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.29 (s, 4H), 6.64 (d, *J* = 16.0 Hz, 1H), 6.02 (dd, *J* = 16.1, 6.1 Hz, 1H), 4.19 (t, *J* = 7.5 Hz, 1H), 3.85 – 3.51 (m, 5H), 3.35 (t, *J* = 4.5 Hz, 1H), 1.28 (s, 9H).

**$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 150.7, 133.5, 132.0, 126.1, 125.3, 124.3, 76.0, 70.8, 66.4, 66.1, 34.4, 31.1.

**HRMS (ESI-MS):** calculated $C_{16}H_{23}O_2^+$ ($[M+H]^+$): 247.16926, found: 247.16901.

### methyl 2-(2-iodobenzamido)propanoate (6j) [3]

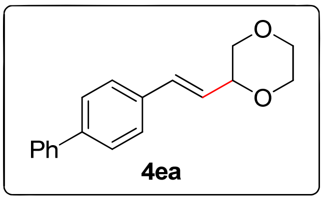


**6j**

**$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.85 (d, *J* = 8.1 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.17 – 7.02 (m, 1H), 6.56 (s, 1H), 4.77 (p, *J* = 7.2 Hz, 1H), 3.77 (s, 3H), 1.54 (d, *J* = 7.2 Hz, 3H).

**$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 173.1, 168.6, 141.5, 139.9, 131.3, 128.4, 128.2, 92.4, 52.6, 48.6, 18.4.

### (E)-2-(2-([1,1'-biphenyl]-4-yl)vinyl)-1,4-dioxane (4ea)


**4ea**

Following the general procedure: $Re_2(CO)_{10}$ (16.4 mg, 0.025 mmol, 2.5 mol%) was added into an oven-dried reaction vessel with Teflon screw cap under nitrogen atmosphere. Then, hypervalent iodine(III) reagent **3j** (1.56 g, 4.0 mmol, 4.0 eq.), 1,4-dioxane (20 mL, 0.05 M), and 4-vinyl-1,1'-biphenyl **1e** (180 mg, 1 mmol, 1.0 eq.) were subjected in sequence to the reaction tube. The reaction mixture was stirred in an oil bath at 120 °C for 4 h. Then the reaction mixture was cooled down to room temperature, diluted with $CH_2Cl_2$ (5 mL), and filtered through a short pad of silica, which was then washed with $CH_2Cl_2$ (30 mL). After the removal of the volatiles in vacuo, the crude mixture was pre-adsorbed on silica gel and purified by flash column chromatography. The product **4ea** was obtained in 57 % isolated yield as white solid.

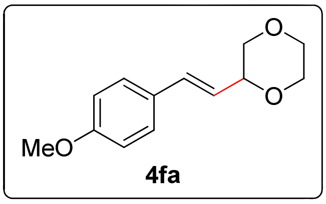
**m.p.:** 165-167 ºC.

**$^1$H NMR (300 MHz, CDCl$_3$)** δ 7.57 (dd, *J* = 10.2, 8.1 Hz, 4H), 7.49 – 7.38 (m, 4H), 7.33 (t, *J* = 7.2 Hz, 1H), 6.72 (d, *J* = 16.1 Hz, 1H), 6.12 (dd, *J* = 16.1, 6.1 Hz, 1H), 4.27 (t, *J* = 7.2 Hz, 1H), 3.91 – 3.61 (m, 5H), 3.49 – 3.36 (m, 1H).

**$^{13}$C NMR (75 MHz, CDCl$_3$)** δ 140.8, 140.7, 135.5, 132.3, 128.9, 127.5, 127.4, 127.1, 125.3, 76.2, 71.1, 66.7, 66.4.

**HRMS (ESI-MS):** calculated $C_{18}H_{19}O_2^+$ ($[M+H]^+$): 267.13796, found: 267.13789.

### (*E*)-2-(4-methoxystyryl)-1,4-dioxane (4fa)


**4fa**

Following the general procedure: $Re_2(CO)_{10}$ (16.4 mg, 0.025 mmol, 2.5 mol%) was added into an oven-dried reaction vessel with Teflon screw cap under nitrogen atmosphere. Then, hypervalent iodine(III) reagent **3j** (1.56 g, 4.0 mmol, 4.0 eq.), 1,4-dioxane (20 mL, 0.05 M), and 1-methoxy-4-vinylbenzene **1f** (134 mg, 1 mmol, 1.0 eq.) were subjected in sequence to the reaction tube. The reaction mixture was stirred in an oil bath at 120 °C for 4 h. Then the reaction mixture was cooled down to room temperature, diluted with $CH_2Cl_2$ (5 mL), and filtered through a short pad of silica, which was then washed with $CH_2Cl_2$ (30 mL). After the removal of the volatiles in vacuo, the crude mixture was pre-adsorbed on silica gel and purified by flash column chromatography. The product **4fa** was obtained in 59 % isolated yield as white solid.

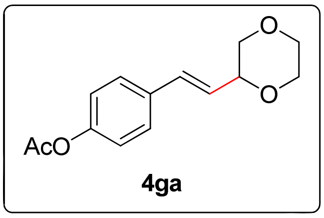
**m.p.:** 111-113 ºC.

**$^1$H NMR (300 MHz, CDCl$_3$)** δ 7.31 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 6.62 (d, *J* = 16.1 Hz, 1H), 5.94 (dd, *J* = 16.1, 6.4 Hz, 1H), 4.21 (t, *J* = 7.5 Hz, 1H), 3.89 – 3.59 (m, 8H), 3.41 (t, *J* = 10.8 Hz, 1H).

**$^{13}$C NMR (75 MHz, CDCl$_3$)** δ 159.6, 132.5, 129.2, 127.8, 122.9, 114.1, 76.4, 71.1, 66.7, 66.4, 55.4.

**HRMS (ESI-MS):** calculated $C_{13}H_{17}O_3^+$ ([M+H]$^+$): 221.11722, found: 221.11746.

**(*E*)-4-(2-(1,4-dioxan-2-yl)vinyl)phenyl acetate (4ga)**



**4ga**

Following the general procedure: $Re_2(CO)_{10}$ (16.4 mg, 0.025 mmol, 2.5 mol%) was added into an oven-dried reaction vessel with Teflon screw cap under nitrogen atmosphere. Then, hypervalent iodine(III) reagent **3j** (1.56 g, 4.0 mmol, 4.0 eq.), 1,4-dioxane (20 mL, 0.05 M), and 4-vinylphenyl acetate **1g** (162 mg, 1 mmol, 1.0 eq.) were subjected in sequence to the reaction tube. The reaction mixture was stirred in an oil bath at 120 °C for 4 h. Then the reaction mixture was cooled down to room temperature, diluted with $CH_2Cl_2$ (5 mL), and filtered through a short pad of silica, which was then washed with $CH_2Cl_2$ (30 mL). After the removal of the volatiles in vacuo, the crude mixture was pre-adsorbed on silica gel and purified by flash column chromatography. The product **4ga** was obtained in 73 % isolated yield as white solid.

**m.p.:** 95-97 ºC.

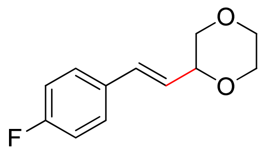
**$^1$H NMR (300 MHz, CDCl$_3$)** δ 7.37 (d, *J* = 8.5 Hz, 2H), 7.04 (d, *J* = 8.5 Hz, 2H), 6.66 (d, *J* = 16.1 Hz, 1H), 6.03 (dd, *J* = 16.1, 6.1 Hz, 1H), 4.26 – 4.21 (m, 1H), 3.91 – 3.60 (m, 5H), 3.40 (t, *J* = 6.0 Hz, 1H), 2.29 (s, 3H).

**$^{13}$C NMR (75 MHz, CDCl$_3$)** δ 169.5, 150.4, 134.3, 131.7, 127.6, 125.5, 121.8, 76.0,

71.0, 66.7, 66.4, 21.2.

**HRMS (ESI-MS):** calculated $C_{14}H_{17}O_4^+$ ($[M+H]^+$): 249.11214, found: 249.11221.

### (*E*)-2-(4-fluorostyryl)-1,4-dioxane (4ha)



**4ha**

Following the general procedure: $Re_2(CO)_{10}$ (16.4 mg, 0.025 mmol, 2.5 mol%) was added into an oven-dried reaction vessel with Teflon screw cap under nitrogen atmosphere. Then, hypervalent iodine(III) reagent **3j** (1.56 g, 4.0 mmol, 4.0 eq.), 1,4-dioxane (20 mL, 0.05 M), and 1-fluoro-4-vinylbenzene **1h** (122 mg, 1 mmol, 1.0 eq.) were subjected in sequence to the reaction tube. The reaction mixture was stirred in an oil bath at 120 °C for 4 h. Then the reaction mixture was cooled down to room temperature, diluted with $CH_2Cl_2$ (5 mL), and filtered through a short pad of silica, which was then washed with $CH_2Cl_2$ (30 mL). After the removal of the volatiles in vacuo, the crude mixture was pre-adsorbed on silica gel and purified by flash column chromatography. The product **4ha** was obtained in 49 % isolated yield as white solid.

**m.p.:** 63-64 ºC.

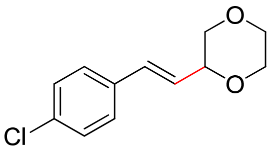
**$^1$H NMR (300 MHz, CDCl$_3$)** δ 7.33 (dd, *J* = 8.3, 5.6 Hz, 2H), 7.00 (t, *J* = 8.6 Hz, 2H), 6.65 (d, *J* = 16.1 Hz, 1H), 5.99 (dd, *J* = 16.1, 6.1 Hz, 1H), 4.23 (t, *J* = 7.4 Hz, 1H), 3.91 – 3.60 (m, 5H), 3.41 (t, *J* = 10.8 Hz, 1H).

**$^{13}$C NMR (75 MHz, CDCl$_3$)** δ 162.6, 132.7, 131.6, 128.2, 125.0, 115.6, 76.1, 71.0, 66.7, 66.4.

**$^{19}$F- NMR (471 MHz, CDCl$_3$)** δ -113.89.

**HRMS (ESI-MS):** calculated $C_{12}H_{14}O_2F^+$ ($[M+H]^+$): 209.09723, found: 209.09744.

### (*E*)-2-(4-chlorostyryl)-1,4-dioxane (4ia)



**4ia**

Following the general procedure: $Re_2(CO)_{10}$ (16.4 mg, 0.025 mmol, 2.5 mol%) was added into an oven-dried reaction vessel with Teflon screw cap under nitrogen atmosphere. Then, hypervalent iodine(III) reagent **3j** (1.56 g, 4.0 mmol, 4.0 eq.), 1,4-dioxane (20 mL, 0.05 M), and 1-chloro-4-vinylbenzene **1i** (138 mg, 1 mmol, 1.0 eq.) were subjected in sequence to the reaction tube. The reaction mixture was stirred in an oil bath at 120 °C for 4 h. Then the reaction mixture was cooled down to room temperature, diluted with $CH_2Cl_2$ (5 mL), and filtered through a short pad of silica, which was then washed with $CH_2Cl_2$ (30 mL). After the removal of the volatiles in vacuo, the crude mixture was pre-adsorbed on silica gel and purified by flash column chromatography. The product **4ia** was obtained in 68 % isolated yield as white solid.

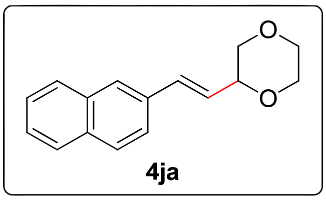
**m.p.:** 86-88 ºC.

**$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.28 – 7.24 (m, 4H), 6.64 (dd, $J$ = 16.1, 1.2 Hz, 1H), 6.05 (dd, $J$ = 16.1, 6.0 Hz, 1H), 4.28 – 4.19 (m, 1H), 3.88 – 3.75 (m, 3H), 3.75 – 3.60 (m, 2H), 3.40 (t, $J$ = 4.5 Hz, 1H).

**$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 135.0, 133.7, 131.4, 128.9, 127.8, 125.9, 76.0, 71.0, 66.7, 66.4.

**HRMS (ESI-MS):** calculated $C_{12}H_{14}O_2Cl^+$ ($[M+H]^+$): 225.06768, found: 225.06781.

**(*E*)-2-(2-(naphthalen-2-yl)vinyl)-1,4-dioxane (4ja)**



**4ja**

Following the general procedure: $Re_2(CO)_{10}$ (16.4 mg, 0.025 mmol, 2.5 mol%) was added into an oven-dried reaction vessel with Teflon screw cap under nitrogen atmosphere. Then, hypervalent iodine(III) reagent **3j** (1.56 g, 4.0 mmol, 4.0 eq.), 1,4-dioxane (20 mL, 0.05 M), and 2-vinylnaphthalene **1j** (154 mg, 1 mmol, 1.0 eq.) were subjected in sequence to the reaction tube. The reaction mixture was stirred in an oil bath at 120 °C for 4 h. Then the reaction mixture was cooled down to room temperature, diluted with $CH_2Cl_2$ (5 mL), and filtered through a short pad of silica, which was then washed with $CH_2Cl_2$ (30 mL). After the removal of the volatiles in vacuo, the crude mixture was pre-adsorbed on silica gel and purified by flash column chromatography. The product **4ja** was obtained in 60 % isolated yield as white solid.

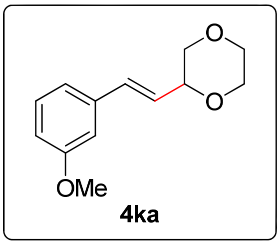
**m.p.:** 104-105 ºC.

**$^1$H NMR (300 MHz, CDCl$_3$)** δ 7.89 – 7.67 (m, 4H), 7.57 (d, *J* = 8.5 Hz, 1H), 7.44 (p, *J* = 6.7 Hz, 2H), 6.84 (d, *J* = 16.1 Hz, 1H), 6.20 (dd, *J* = 16.1, 6.2 Hz, 1H), 4.30 (t, *J* = 7.2 Hz, 1H), 3.95 – 3.62 (m, 5H), 3.46 (t, *J* = 10.8 Hz, 1H).

**$^{13}$C NMR (75 MHz, CDCl$_3$)** δ 134.0, 133.6, 133.3, 132.9, 128.4, 128.2, 127.8, 126.9, 126.4, 126.2, 125.6, 123.5, 76.3, 71.1, 66.8, 66.5.

**HRMS (ESI-MS):** calculated $C_{16}H_{17}O_2^+$ ($[M+H]^+$): 241.12231, found: 241.12248.

**(E)-2-(3-methoxystyryl)-1,4-dioxane (4ka)**



**4ka**

Following the general procedure: $Re_2(CO)_{10}$ (16.4 mg, 0.025 mmol, 2.5 mol%) was added into an oven-dried reaction vessel with Teflon screw cap under nitrogen atmosphere. Then, hypervalent iodine (III) reagent **3j** (1.56 g, 4.0 mmol, 4.0 eq.), 1,4-dioxane (20 mL, 0.05 M), and 1-methoxy-3-vinylbenzene **1k** (134 mg, 1 mmol, 1.0 eq.) were subjected in sequence to the reaction tube. The reaction mixture was stirred in an oil bath at 120 °C for 4 h. Then the reaction mixture was cooled down to room temperature, diluted with $CH_2Cl_2$ (5 mL), and filtered through a short pad of silica, which was then washed with $CH_2Cl_2$ (30 mL). After the removal of the volatiles in vacuo, the crude mixture was pre-adsorbed on silica gel and purified by flash column chromatography. The product **4ka** was obtained in 70 % isolated yield as colorless oil.

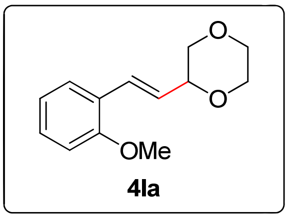
**$^1$H NMR (300 MHz, CDCl$_3$)** δ 7.26 – 7.22 (m, 1H), 6.96 (d, *J* = 7.7 Hz, 1H), 6.91 (s, 1H), 6.82 – 6.78 (m, 1H), 6.65 (d, *J* = 16.1 Hz, 1H), 6.07 (dd, *J* = 16.1, 6.1 Hz, 1H), 4.30 – 4.19 (m, 1H), 3.92 – 3.60 (m, 8H), 3.42 (t, *J* = 6.0 Hz, 1H).

**$^{13}$C NMR (75 MHz, CDCl$_3$)** δ 159.9, 138.0, 132.7, 129.7, 125.6, 119.3, 113.8, 111.9, 76.1, 71.0, 66.7, 66.4, 55.3.

**HRMS (ESI-MS):** calculated $C_{13}H_{17}O_3^+$ ($[M+H]^+$): 221.11722, found: 211.11734.

**(*E*)-2-(2-methoxystyryl)-1,4-dioxane (4la)**

Following the general procedure: $Re_2(CO)_{10}$ (16.4 mg, 0.025 mmol, 2.5 mol%) was added into an oven-dried reaction vessel with Teflon screw cap under nitrogen


**4la**

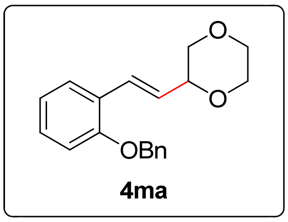
atmosphere. Then, hypervalent iodine(III) reagent **3j** (1.56 g, 4.0 mmol, 4.0 eq.), 1,4-dioxane (20 mL, 0.05 M) and 1-methoxy-2-vinylbenzene **1l** (134 mg, 1 mmol, 1.0 eq.) were subjected in sequence to the reaction tube. The reaction mixture was stirred in an oil bath at 120 °C for 4 h. Then the reaction mixture was cooled down to room temperature, diluted with $CH_2Cl_2$ (5 mL), and filtered through a short pad of silica, which was then washed with $CH_2Cl_2$ (30 mL). After the removal of the volatiles in vacuo, the crude mixture was pre-adsorbed on silica gel and purified by flash column chromatography. The product **4la** was obtained in 49 % isolated yield as colorless oil.

**$^1$H NMR (300 MHz, CDCl$_3$)** δ 7.41 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.28 – 7.17 (m, 1H), 7.05 – 6.82 (m, 3H), 6.11 (dd, *J* = 16.2, 6.4 Hz, 1H), 4.30 – 4.20 (m, 1H), 3.90 – 3.60 (m, 8H), 3.43 (t, *J* = 6.0 Hz, 1H).

**$^{13}$C NMR (75 MHz, CDCl$_3$)** δ 157.0, 129.1, 127.9, 127.1, 125.9, 125.5, 120.7, 110.9, 76.7, 71.1, 66.7, 66.4, 55.5.

**HRMS (ESI-MS):** calculated $C_{13}H_{17}O_3^+$ ($[M+H]^+$): 221.11722, found: 221.11743.

**(E)-2-(2-(benzyloxy)styryl)-1,4-dioxane (4ma)**


**4ma**

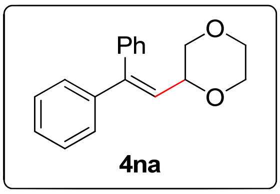
Following the general procedure: $Re_2(CO)_{10}$ (16.4 mg, 0.025 mmol, 2.5 mol%) was added into an oven-dried reaction vessel with Teflon screw cap under nitrogen atmosphere. Then, hypervalent iodine(III) reagent **3j** (1.56 g, 4.0 mmol, 4.0 eq.), 1,4-dioxane (20 mL, 0.05 M), and 1-(benzyloxy)-2-vinylbenzene **1m** (210 mg, 1 mmol, 1.0 eq.) were subjected in sequence to the reaction tube. The reaction mixture was stirred in an oil bath at 120 °C for 4 h. Then the reaction mixture was cooled down to room temperature, diluted with $CH_2Cl_2$ (5 mL), and filtered through a short pad of silica, which was then washed with $CH_2Cl_2$ (30 mL). After the removal of the volatiles in vacuo, the crude mixture was pre-adsorbed on silica gel and purified by flash column chromatography. The product **4ma** was obtained in 61 % isolated yield as colorless oil.

**$^1$H NMR (300 MHz, CDCl$_3$)** δ 7.48 – 7.27 (m, 6H), 7.23 – 7.13 (m, 1H), 7.06 (d, *J* = 16.2 Hz, 1H), 6.95 – 6.85 (m, 2H), 6.12 (dd, *J* = 16.2, 6.6 Hz, 1H), 5.08 (s, 2H), 4.29 – 4.17 (m, 1H), 3.87 – 3.57 (m, 5H), 3.41 (t, *J* = 6.0 Hz, 1H).

**$^{13}$C NMR (75 MHz, CDCl$_3$)** δ 156.1, 137.1, 129.0, 128.6, 128.0, 127.3, 127.1, 126.0, 125.8, 121.0, 112.6, 100.0, 76.7, 71.0, 70.4, 66.6, 66.4.

**HRMS (ESI-MS):** calculated $C_{19}H_{21}O_3^+$ ([M+H]$^+$): 297.14852, found: 297.14880.

**2-(2,2-diphenylvinyl)-1,4-dioxane (4na)**



**4na**

Following the general procedure: $Re_2(CO)_{10}$ (16.4 mg, 0.025 mmol, 2.5 mol%) was added into an oven-dried reaction vessel with Teflon screw cap under nitrogen atmosphere. Then, hypervalent iodine(III) reagent **3j** (1.56 g, 4.0 mmol, 4.0 eq.), 1,4-dioxane (20 mL, 0.05 M), and ethene-1,1-diyldibenzene **1n** (180 mg, 1 mmol, 1.0 eq.) were subjected in sequence to the reaction tube. The reaction mixture was stirred in an oil bath at 120 °C for 4 h. Then the reaction mixture was cooled down to room temperature, diluted with $CH_2Cl_2$ (5 mL), and filtered through a short pad of silica, which was then washed with $CH_2Cl_2$ (30 mL). After the removal of the volatiles in vacuo, the crude mixture was pre-adsorbed on silica gel and purified by flash column chromatography. The product **4na** was obtained in 81 % isolated yield as white solid.

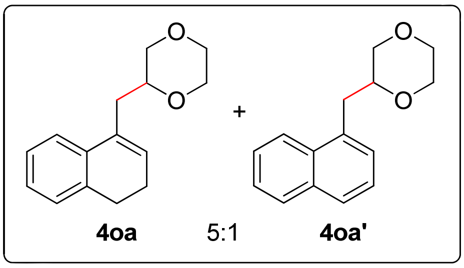
**m.p.:** 98-99 ºC.

**$^1$H NMR (300 MHz, CDCl$_3$)** δ 7.36 – 7.33 (m, 3H), 7.26 – 7.17 (m, 7H), 5.98 – 5.89 (m, 1H), 4.18 – 4.06 (m, 1H), 3.72 (t, *J* = 9.0 Hz, 2H), 3.61 (d, *J* = 6.9 Hz, 3H), 3.46 (t, *J* = 10.7 Hz, 1H).

**$^{13}$C NMR (75 MHz, CDCl$_3$)** δ 146.8, 141.4, 139.1, 129.5, 128.3, 128.2, 127.9, 127.7, 127.6, 124.2, 73.7, 70.3, 66.1, 66.1.

**HRMS (ESI-MS):** calculated $C_{18}H_{19}O_2^+$ ([M+H]$^+$): 267.13796, found: 267.13803.

**2-((3,4-dihydronaphthalen-1-yl)methyl)-1,4-dioxane (4oa) and (*E*)-2-((3,4-dihydronaphthalen-1(2*H*)-ylidene)methyl)-1,4-dioxane (4oa')**



Following the general procedure with slight modifications:. $Re_2(CO)_{10}$ (32.8 mg, 0.05 mmol, 5 mol%) was added into an oven-dried reaction vessel with Teflon screw cap under nitrogen atmosphere. Then, hypervalent iodine(III) reagent **3j** (1.56 g, 4.0 mmol, 4.0 eq.), 1,4-dioxane (30 mL, 0.033 M), and 1-methylene-1,2,3,4-tetrahydronaphthalene **1o** (144 mg, 1 mmol, 1.0 eq.) were subjected in sequence to the reaction tube. The reaction mixture was stirred in an oil bath at 150 °C for 4 h. Then the reaction mixture was cooled down to room temperature, diluted with $CH_2Cl_2$ (5 mL), and filtered through a short pad of silica, which was then washed with $CH_2Cl_2$ (30 mL). After the removal of the volatiles in vacuo, the crude mixture was pre-adsorbed on silica gel and purified by flash column chromatography. The product **4oa** and **4oa'** was obtained in 65 % combined isolated yield with a ratio of 5:1 as colorless oil. The ratio of two products was identified by GC-MS.

The data for the major product **4oa**:

**$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.29 – 7.17 (m, 2H), 7.14 (dd, $J$ = 6.7, 5.3 Hz, 2H), 5.90 (t, $J$ = 4.2 Hz, 1H), 3.85 – 3.52 (m, 6H), 3.31 (t, $J$ = 10.4 Hz, 1H), 2.71 (dd, $J$ = 15.9, 7.5 Hz, 3H), 2.42 (dd, $J$ = 14.4, 7.3 Hz, 1H), 2.24 (dd, $J$ = 12.2, 7.7 Hz, 2H).

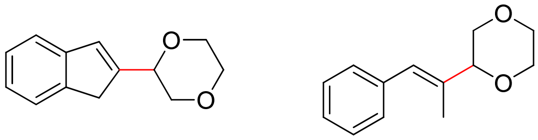
**$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 136.8, 134.5, 132.1, 127.8, 127.7, 127.0, 126.5, 122.8, 73.7, 71.4, 67.0, 66.6, 35.8, 28.4, 23.2.

**HRMS (ESI-MS):** calculated $C_{15}H_{19}O_2^+$ ($[M+H]^+$): 231.13796, found: 231.13791.

The HRMS data for the minor product **4oa'**:

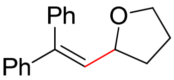
**HRMS (ESI-MS):** calculated $C_{15}H_{17}O_2^+$ ($[M+H]^+$): 229.12231, found: 229.12233.

It should be pointed out that 1,2-disubstituted olefins such as 1*H*-indine and (Z)-prop-1-en-1-ylbenzene showed low reactivity in this reaction. We proposed that the steric hindrance in the step of C-C bond formation might account for the observed low reactivity of these substrates.



15% 10%

### 2-(2,2-diphenylvinyl)tetrahydrofuran (4nb)



**4nb**

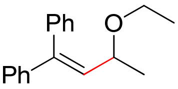
Following the general procedure with slight modifications: $Re_2(CO)_{10}$ (32.8 mg, 0.05 mmol, 5 mol%) was added into an oven-dried reaction vessel with Teflon screw cap under nitrogen atmosphere. Then, hypervalent iodine(III) reagent **3j** (1.56 g, 4.0 mmol, 4.0 eq.), THF **2b** (30 mL, 0.033 M) and ethene-1,1-diyldibenzene **1n** (180 mg, 1 mmol, 1.0 eq.) were subjected in sequence to the reaction tube. The reaction mixture was stirred in an oil bath at 150 °C for 4 h. Then the reaction mixture was cooled down to room temperature, diluted with $CH_2Cl_2$ (5 mL), and filtered through a short pad of silica, which was then washed with $CH_2Cl_2$ (30 mL). After the removal of the volatiles in vacuo, the crude mixture was pre-adsorbed on silica gel and purified by flash column chromatography. The product **4nb** was obtained in 88 % isolated yield as colorless oil.

**$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.40 – 7.28 (m, 3H), 7.28 – 7.15 (m, 7H), 6.06 (d, $J$ = 9.0 Hz, 1H), 4.29 (dd, $J$ = 14.8, 8.2 Hz, 1H), 3.93 (dd, $J$ = 14.5, 7.0 Hz, 1H), 3.71 (dd, $J$ = 13.7, 7.8 Hz, 1H), 2.11 – 1.90 (m, 2H), 1.90 – 1.62 (m, 2H).

**$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 143.8, 142.1, 139.5, 130.0, 129.8, 128.2, 127.7, 127.5, 127.4, 76.7, 68.1, 33.2, 26.5.

**HRMS (ESI-MS):** calculated $C_{18}H_{19}O^+$ ($[M+H]^+$): 251.14304, found: 251.14301.

### (3-ethoxybut-1-ene-1,1-diyl)dibenzene (4nc)



**4nc**

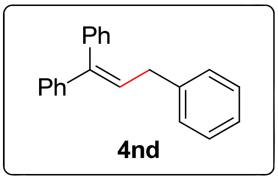
Following the general procedure: $Re_2(CO)_{10}$ (16.4 mg, 0.025 mmol, 2.5 mol%) was added into an oven-dried reaction vessel with Teflon screw cap under nitrogen atmosphere. Then, hypervalent iodine(III) reagent **3j** (1.56 g, 4.0 mmol, 4.0 eq.), diethyl ether **2c** (20 mL, 0.05 M) and ethene-1,1-diyldibenzene **1n** (180 mg, 1 mmol, 1.0 eq.) were subjected in sequence to the reaction tube. The reaction mixture was stirred in an oil bath at 120 °C for 4 h. Then the reaction mixture was cooled down to room temperature, diluted with $CH_2Cl_2$ (5 mL), and filtered through a short pad of silica, which was then washed with $CH_2Cl_2$ (30 mL). After the removal of the volatiles in vacuo, the crude mixture was pre-adsorbed on silica gel and purified by flash column chromatography. The product **4nc** was obtained in 50 % isolated yield as colorless oil.

**$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.42 – 7.29 (m, 3H), 7.25 (s, 5H), 7.20 – 7.11 (m, 2H), 6.03 (d, *J* = 9.2 Hz, 1H), 3.96 (dq, *J* = 9.2, 6.3 Hz, 1H), 3.60 – 3.44 (m, 1H), 3.22 (dq, *J* = 9.1, 7.0 Hz, 1H), 1.29 (d, *J* = 6.3 Hz, 3H), 1.12 (t, *J* = 7.0 Hz, 3H).

**$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 143.3, 141.7, 139.7, 131.8, 129.8, 128.4, 128.3, 127.6, 127.4, 127.3, 72.5, 63.5, 21.8, 15.6.

**HRMS (EI-MS):** calculated $C_{18}H_{20}O$: 252.1514, found: 252.1513.

### prop-1-ene-1,1,3-triyltribenzene (4nd)



**4nd**

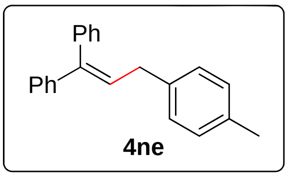
Following the general procedure with slight modifications: $Re_2(CO)_{10}$ (32.8 mg, 0.05 mmol, 5 mol%) was added into an oven-dried reaction vessel with Teflon screw cap under nitrogen atmosphere. Then, hypervalent iodine(III) reagent **3j** (1.56 g, 4.0 mmol, 4.0 eq.), toluene **2d** (30 mL, 0.033 M) and ethene-1,1-diyldibenzene **1n** (180 mg, 1 mmol, 1.0 eq.) were subjected in sequence to the reaction tube. The reaction mixture was stirred in an oil bath at 150 °C for 4 h. Then the reaction mixture was cooled down to room temperature, diluted with $CH_2Cl_2$ (5 mL), and filtered through a short pad of silica, which was then washed with $CH_2Cl_2$ (30 mL). After the removal of the volatiles in vacuo, the crude mixture was pre-adsorbed on silica gel and purified by flash column chromatography. The product **4nd** was obtained in 62 % isolated yield as colorless oil.

**$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.42 – 7.13 (m, 15H), 6.26 (t, *J* = 7.6 Hz, 1H), 3.46 (d, *J* = 7.6 Hz, 2H).

**$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 142.7, 142.6, 141.1, 140.0, 130.1, 128.63, 128.55, 128.4, 128.3, 127.9, 127.5, 127.3, 127.2, 126.1, 36.1.

**HRMS (ESI-MS):** calculated $C_{21}H_{19}^+$ ($[M+H]^+$): 271.14813, found: 271.14822.

### (3-(p-tolyl)prop-1-ene-1,1-diyl)dibenzene (4ne)



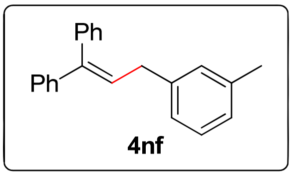
Following the general procedure with slight modifications: $Re_2(CO)_{10}$ (32.8 mg, 0.05 mmol, 5 mol%) was added into an oven-dried reaction vessel with Teflon screw cap under nitrogen atmosphere. Then, hypervalent iodine(III) reagent **3j** (1.56 g, 4.0 mmol, 4.0 eq.), *p*-xylene **2e** (5 mL, 0.2 M) and ethene-1,1-diyldibenzene **1n** (1 mmol, 1.0 eq.) were subjected in sequence to the reaction tube. The reaction mixture was stirred in an oil bath at 150 °C for 4 h. Then the reaction mixture was cooled down to room temperature, diluted with $CH_2Cl_2$ (5 mL), and filtered through a short pad of silica, which was then washed with $CH_2Cl_2$ (30 mL). After the removal of the volatiles in vacuo, the crude mixture was pre-adsorbed on silica gel and purified by flash column chromatography. The product **4ne** was obtained in 64 % isolated yield as colorless oil.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.37 (t, $J$ = 7.0 Hz, 2H), 7.33 – 7.28 (m, 1H), 7.24 (m, 7H), 7.09 (s, 4H), 6.25 (t, $J$ = 7.6 Hz, 1H), 3.43 (d, $J$ = 7.6 Hz, 2H), 2.31 (s, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 142.6, 142.4, 140.0, 138.0, 135.6, 130.1, 129.3, 128.4, 128.23, 128.21, 127.5, 127.2, 127.1, 35.6, 21.2.

**HRMS (EI-MS):** calculated $C_{22}H_{20}$: 284.1565, found: 284.1563.

### (2,2-diphenylvinyl)cyclooctane (4nf)



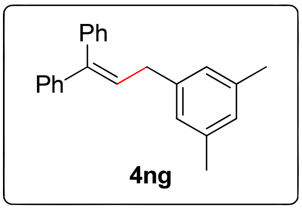
Following the general procedure with slight modifications: $Re_2(CO)_{10}$ (32.8 mg, 0.05 mmol, 5 mol%) was added into an oven-dried reaction vessel with Teflon screw cap under nitrogen atmosphere. Then, hypervalent iodine(III) reagent **3j** (1.56 g, 4.0 mmol, 4.0 eq.), *m*-xylene **2f** (5 mL, 0.2 M) and ethene-1,1-diyldibenzene **1n** (1 mmol, 1.0 eq.) were subjected in sequence to the reaction tube. The reaction mixture was stirred in an oil bath at 150 °C for 4 h. Then the reaction mixture was cooled down to room temperature, diluted with $CH_2Cl_2$ (5 mL), and filtered through a short pad of silica, which was then washed with $CH_2Cl_2$ (30 mL). After the removal of the volatiles in vacuo, the crude mixture was pre-adsorbed on silica gel and purified by flash column chromatography. The product **4nf** was obtained in 67 % isolated yield as colorless oil.

**$^1$H NMR (400 MHz, CDCl$_3$)** δ 7.39 (t, *J* = 7.1 Hz, 2H), 7.33 (d, *J* = 7.1 Hz, 1H), 7.24 (m, 7H), 7.17 (t, *J* = 7.7 Hz, 1H), 7.01 (s, 3H), 6.26 (t, *J* = 7.6 Hz, 1H), 3.44 (d, *J* = 7.6 Hz, 2H), 2.33 (s, 3H).

**$^{13}$C NMR (100 MHz, CDCl$_3$)** δ 142.6, 142.5, 141.0, 140.0, 138.2, 130.1, 129.3, 128.5, 128.4, 128.3, 128.1, 127.5, 127.3, 127.2, 126.9, 125.6, 36.0, 21.6.

**HRMS (EI-MS):** calculated $C_{22}H_{20}$: 284.1565, found: 284.1562.

### (3-(3,5-dimethylphenyl)prop-1-ene-1,1-diyl)dibenzene (4ng)



4ng

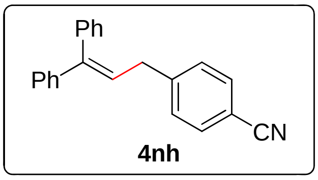
Following the general procedure with slight modifications: $Re_2(CO)_{10}$ (32.8 mg, 0.05 mmol, 5 mol%) was added into an oven-dried reaction vessel with Teflon screw cap under nitrogen atmosphere. Then, hypervalent iodine(III) reagent **3j** (1.56 g, 4.0 mmol, 4.0 eq.), mesitylene **2g** (30 mL, 0.033 M) and ethene-1,1-diyldibenzene **1n** (180 mg, 1 mmol, 1.0 eq.) were subjected in sequence to the reaction tube. The reaction mixture was stirred in an oil bath at 150 °C for 4 h. Then the reaction mixture was cooled down to room temperature, diluted with $CH_2Cl_2$ (5 mL), and filtered through a short pad of silica, which was then washed with $CH_2Cl_2$ (30 mL). After the removal of the volatiles in vacuo, the crude mixture was pre-adsorbed on silica gel and purified by flash column chromatography. The product **4ng** was obtained in 66 % isolated yield as colorless oil.

**$^1$H NMR (300 MHz, CDCl$_3$)** δ 7.33 (dd, *J* = 14.3, 6.1 Hz, 3H), 7.23 (t, *J* = 6.1 Hz, 7H), 6.81 (d, *J* = 6.0 Hz, 3H), 6.25 (t, *J* = 7.5 Hz, 1H), 3.39 (d, *J* = 7.5 Hz, 2H), 2.27 (s, 6H).

**$^{13}$C NMR (75 MHz, CDCl$_3$)** δ 142.6, 142.3, 141.0, 140.0, 138.1, 130.1, 128.4, 128.23, 128.18, 127.8, 127.5, 127.2, 127.1, 126.4, 35.9, 21.4.

**HRMS (EI-MS):** calculated $C_{23}H_{22}$: 298.1722, found: 298.1724.

### 4-(3,3-diphenylallyl)benzonitrile (4nh)



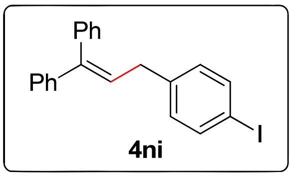
Following the general procedure with slight modifications: $Re_2(CO)_{10}$ (32.8 mg, 0.05 mmol, 5 mol%) was added into an oven-dried reaction vessel with Teflon screw cap under nitrogen atmosphere. Then, hypervalent iodine(III) reagent **3j** (1.56 g, 4.0 mmol, 4.0 eq.), 4-methylbenzonitrile **2h** (5 mL, 0.2 M) and ethene-1,1-diyldibenzene **1n** (1 mmol, 1.0 eq.) were subjected in sequence to the reaction tube. The reaction mixture was stirred in an oil bath at 150 °C for 4 h. Then the reaction mixture was cooled down to room temperature, diluted with $CH_2Cl_2$ (5 mL), and filtered through a short pad of silica, which was then washed with $CH_2Cl_2$ (30 mL). After the removal of the volatiles in vacuo, the crude mixture was pre-adsorbed on silica gel and purified by flash column chromatography. The product **4nh** was obtained in 69 % isolated yield as colorless oil.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.56 (d, $J$ = 7.9 Hz, 2H), 7.39 (t, $J$ = 7.3 Hz, 2H), 7.35 (d, $J$ = 6.8 Hz, 1H), 7.30 – 7.22 (m, 7H), 7.20 (d, $J$ = 7.5 Hz, 2H), 6.20 (t, $J$ = 7.6 Hz, 1H), 3.51 (d, $J$ = 7.6 Hz, 2H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 146.7, 144.1, 142.0, 139.5, 132.4, 129.8, 129.3, 128.6, 128.3, 127.5, 127.4, 125.6, 119.1, 110.0, 36.1.

**HRMS (EI-MS):** calculated $C_{22}H_{17}N$: 295.1361, found: 295.1357.

**(3-(4-iodophenyl)prop-1-ene-1,1-diyl)dibenzene (4ni)**



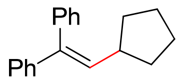
Following the general procedure with slight modification: $Re_2(CO)_{10}$ (32.8 mg, 0.05 mmol, 5 mol%) was added into an oven-dried reaction vessel with Teflon screw cap under nitrogen atmosphere. Then, hypervalent iodine(III) reagent **3j** (1.56 g, 4.0 mmol, 4.0 eq.), 1-iodo-4-methylbenzene **2i** (5 mL, 0.2 M) and ethene-1,1-diyldibenzene **1n** (1 mmol, 1.0 eq.) were subjected in sequence to the reaction tube. The reaction mixture was stirred in an oil bath at 150 °C for 4 h. Then the reaction mixture was cooled down to room temperature, diluted with $CH_2Cl_2$ (5 mL), and filtered through a short pad of silica, which was then washed with $CH_2Cl_2$ (30 mL). After the removal of the volatiles in vacuo, the crude mixture was pre-adsorbed on silica gel and purified by flash column chromatography. The product **4ni** was obtained in 61 % isolated yield as colorless oil.

**$^1$H NMR (400 MHz, CDCl$_3$)** δ 7.63 – 7.56 (m, 2H), 7.42 – 7.30 (m, 3H), 7.27 – 7.19 (m, 7H), 6.94 (d, *J* = 8.1 Hz, 2H), 6.20 (t, *J* = 7.6 Hz, 1H), 3.40 (d, *J* = 7.6 Hz, 2H).

**$^{13}$C NMR (100 MHz, CDCl$_3$)** δ 143.2, 142.3, 140.8, 139.8, 137.6, 130.6, 130.0, 128.5, 128.3, 127.5, 127.4, 127.3, 127.0, 91.2, 35.6.

**HRMS (EI-MS):** calculated $C_{21}H_{17}I$: 396.0375, found: 396.0371.

### (2-cyclopentylethene-1,1-diyl)dibenzene (4nj)



**4nj**

Following the general procedure with slight modifications: Re$_2$(CO)$_{10}$ (32.8 mg, 0.05 mmol, 5 mol%) was added into an oven-dried reaction vessel with Teflon screw cap under nitrogen atmosphere. Then, hypervalent iodine(III) reagent **3j** (1.56 g, 4.0 mmol, 4.0 eq.), cyclopentane **2j** (10 mL, 0.1 M) and ethene-1,1-diyldibenzene **1n** (1 mmol, 1.0 eq.) were subjected in sequence to the reaction tube. The reaction mixture was stirred in an oil bath at 150 °C for 12 h. Then the reaction mixture was cooled down to room temperature, diluted with CH$_2$Cl$_2$ (5 mL), and filtered through a short pad of silica, which was then washed with CH$_2$Cl$_2$ (30 mL). After the removal of the volatiles in vacuo, the crude mixture was pre-adsorbed on silica gel and purified by flash column chromatography. The product **4nj** was obtained in 91 % isolated yield as colorless oil.

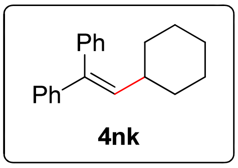
**$^1$H NMR (400 MHz, CDCl$_3$)** δ 7.37 – 7.29 (m, 3H), 7.27 – 7.14 (m, 7H), 5.97 (d, *J* = 10.0 Hz, 1H), 2.56 – 2.51 (m, 1H), 1.80 – 1.70 (m, 2H), 1.69 – 1.65 (m, 2H), 1.52 – 1.46 (m, *J* = 7.5, 3.9 Hz, 2H), 1.45 – 1.28 (m, 2H).

**$^{13}$C NMR (100 MHz, CDCl$_3$)** δ 143.0, 140.7, 140.1, 135.6, 130.1, 128.2, 128.1, 127.4, 126.9, 126.8, 40.6, 34.4, 25.7.

**HRMS (EI-MS):** calculated $C_{19}H_{20}$: 248.1565, found: 248.1569.

### (2-cyclohexylethene-1,1-diyl)dibenzene (4nk)

Following the general procedure with slight modifications: Re$_2$(CO)$_{10}$ (32.8 mg, 0.05 mmol, 5 mol%) was added into an oven-dried reaction vessel with Teflon screw cap



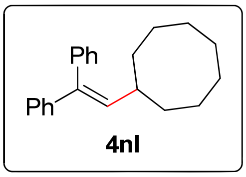
under nitrogen atmosphere. Then, hypervalent iodine(III) reagent **3j** (1.56 g, 4.0 mmol, 4.0 eq.), cyclohexane **2k** (10 mL, 0.1 M) and ethene-1,1-diyldibenzene **1n** (1 mmol, 1.0 eq.) were subjected in sequence to the reaction tube. The reaction mixture was stirred in an oil bath at 150 °C for 12 h. Then the reaction mixture was cooled down to room temperature, diluted with $CH_2Cl_2$ (5 mL), and filtered through a short pad of silica, which was then washed with $CH_2Cl_2$ (30 mL). After the removal of the volatiles in vacuo, the crude mixture was pre-adsorbed on silica gel and purified by flash column chromatography. The product **4nk** was obtained in 95 % isolated yield as colorless oil.

**$^1$H NMR (400 MHz, CDCl$_3$)** δ 7.35 – 7.29 (m, 3H), 7.23 – 7.16 (m, 7H), 5.90 (d, *J* = 9.9 Hz, 1H), 2.25 – 2.04 (m, 1H), 1.77 – 1.52 (m, 5H), 1.17 – 1.15 (m, 5H).

**$^{13}$C NMR (100 MHz, CDCl$_3$)** δ 143.1, 140.7, 139.7, 136.1, 129.9, 128.3, 128.2, 127.3, 126.9, 126.8, 38.4, 33.5, 26.1, 25.7.

**HRMS (EI-MS):** calculated $C_{20}H_{22}$: 262.1722, found: 262.1718.

**(2,2-diphenylvinyl)cyclooctane (4nl)**



Following the general procedure: $Re_2(CO)_{10}$ (32.8 mg, 0.05 mmol, 5 mol%) was added into an oven-dried reaction vessel with Teflon screw cap under nitrogen atmosphere. Then, hypervalent iodine(III) reagent **3j** (1.56 g, 4.0 mmol, 4.0 eq.), cyclooctane **2l** (10 mL, 0.1 M) and ethene-1,1-diyldibenzene **1n** (1 mmol, 1.0 eq.) were subjected in sequence to the reaction tube. The reaction mixture was stirred in an oil bath at 150 °C for 12 h. Then the reaction mixture was cooled down to room temperature, diluted with $CH_2Cl_2$ (5 mL), and filtered through a short pad of silica, which was then washed with $CH_2Cl_2$ (30 mL). After the removal of the volatiles in vacuo, the crude mixture was pre-adsorbed on silica gel and purified by flash column chromatography. The product **4nl** was obtained in 71 % isolated yield as colorless oil.

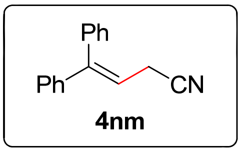
**$^1$H NMR (400 MHz, CDCl$_3$)** δ 7.38 – 7.28 (m, 3H), 7.26 – 7.13 (m, 7H), 6.04 (d, *J* = 10.4 Hz, 1H), 2.51 – 2.30 (m, 1H), 1.67 – 1.64 (m, 4H), 1.53 – 1.37 (m, 10H).

**$^{13}$C NMR (100 MHz, CDCl$_3$)** δ 143.0, 140.7, 138.4, 136.8, 129.9, 128.2, 128.1, 127.3,

126.9, 126.8, 37.5, 32.7, 27.4, 26.5, 25.2.

**HRMS (EI-MS):** calculated $C_{22}H_{26}$: 290.2035, found: 290.2039.

### 4,4-diphenylbut-3-enenitrile (4nm)


**4nm**

Following the general procedure with slight modifications: $Re_2(CO)_{10}$ (32.8 mg, 0.05 mmol, 5 mol%) was added into an oven-dried reaction vessel with Teflon screw cap under nitrogen atmosphere. Then, hypervalent iodine(III) reagent **3j** (1.56 g, 4.0 mmol, 4.0 eq.), acetonitrile **3m** (30 mL, 0.033 M), and ethene-1,1-diyldibenzene **1n** (180 mg, 1 mmol, 1.0 eq.) were subjected in sequence to the reaction tube. The reaction mixture was stirred in an oil bath at 150 °C for 4 h. Then the reaction mixture was cooled down to room temperature, diluted with $CH_2Cl_2$ (5 mL), and filtered through a short pad of silica, which was then washed with $CH_2Cl_2$ (30 mL). After the removal of the volatiles in vacuo, the crude mixture was pre-adsorbed on silica gel and purified by flash column chromatography. The product **4nm** was obtained in 58 % isolated yield as white solid. Meanwhile, the *N*-olefination side product **7j** was obtained in 11% isolated yield.

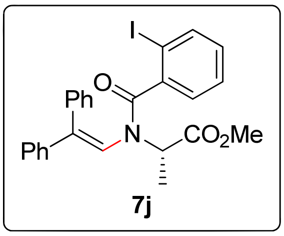
**m.p.:** 104-105 ºC.

**$^1$H NMR (300 MHz, CDCl$_3$)** δ 7.49 – 7.34 (m, 3H), 7.33 – 7.26 (m, 3H), 7.26 – 7.12 (m, 4H), 6.04 (t, *J* = 7.4 Hz, 1H), 3.14 (d, *J* = 7.4 Hz, 2H).

**$^{13}$C NMR (75 MHz, CDCl$_3$)** δ 147.7, 140.8, 138.1, 129.5, 128.9, 128.5, 128.33, 128.27, 127.6, 118.3, 115.6, 18.5..

**HRMS (ESI-MS):** calculated $C_{16}H_{14}N^+$ ($[M+H]^+$): 220.11208, found: 220.11220.

The data for *N*-olefination side product **7j:**


**7j**

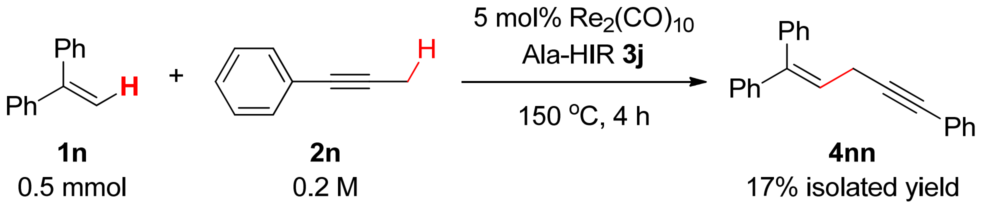
**m.p.:** 161-162 ºC.

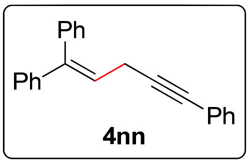
**$^1$H NMR (300 MHz, CDCl$_3$)**δ 7.73 (d, *J* = 7.9 Hz, 1H), 7.32 – 7.31 (m, 3H), 7.26 – 7.25 (m, 3H), 7.10 (ddd, *J* = 10.8, 9.0, 7.2 Hz, 5H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 7.3 Hz, 1H), 6.55 (d, *J* = 3.2 Hz, 1H), 4.66 (d, *J* = 5.9 Hz, 1H), 3.78 (d, *J* = 3.2 Hz, 3H), 1.57 (dd, *J* = 7.1, 3.2 Hz, 3H).

**$^{13}$C NMR (75 MHz, CDCl$_3$)** δ 171.4, 170.1, 141.2, 141.0, 139.2, 137.5, 130.3, 130.1, 129.0, 128.6, 128.4, 128.3, 128.2, 127.9, 127.8, 124.9, 92.3, 56.4, 52.3, 14.7.

**HRMS (ESI-MS):** calculated $C_{25}H_{22}O_3NINa^+$ ($[M+Na]^+$): 534.05366, found: 534.05321.

Of note, we subjected also prop-1-yn-1-ylbenzene **2n** and allylbenzene **2o** to our standard reaction conditions respectively. It turned out that the expected propargylic C-H bond olefination product **4nn** could be obtained from the reaction of **1n** and **2n** in 17% isolated yield while only a small amount of allylic C-H bond olefination product **4no** was detected by GC-MS in the reaction of **1n** and **2o**, which failed to be isolated in pure form.





**4nn**

Following the general procedure with slight modification: $Re_2(CO)_{10}$ (16.4 mg, 0.025 mmol, 5 mol%) was added into an oven-dried reaction vessel with Teflon screw cap under nitrogen atmosphere. Then, hypervalent iodine(III) reagent **3j** (0.78 g, 2.0 mmol, 4.0 eq.), prop-1-yn-1-ylbenzene **2n** (2.5 mL, 0.2 M) and ethene-1,1-diyldibenzene **1n** (0.5 mmol, 1.0 eq.) were subjected in sequence to the reaction tube. The reaction mixture was stirred in an oil bath at 150 °C for 4 h. Then the reaction mixture was cooled down to room temperature, diluted with $CH_2Cl_2$ (5 mL), and filtered through a short pad of silica, which was then washed with $CH_2Cl_2$ (30 mL). After the removal of the volatiles in vacuo, the crude mixture was pre-adsorbed on silica gel and purified by flash column chromatography. The product **4nn** was obtained in 17 % isolated yield as colorless oil.

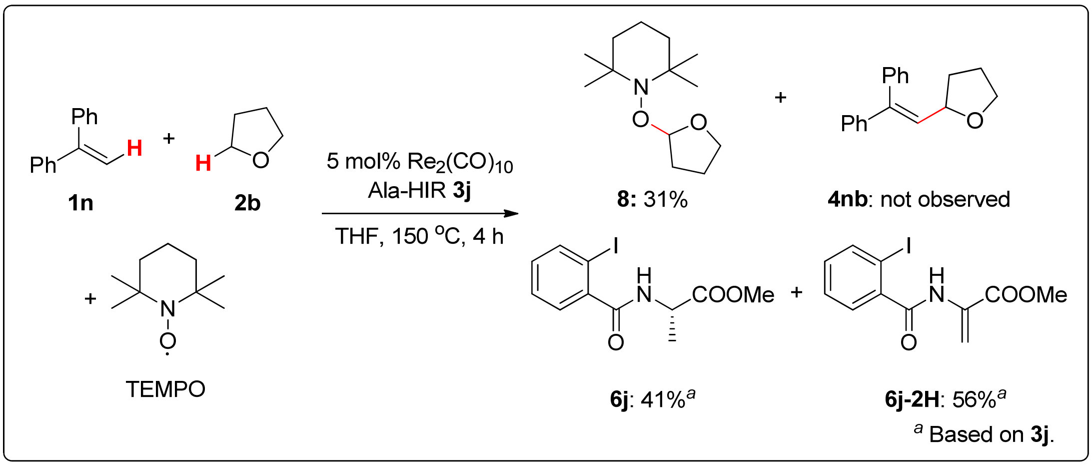
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.40 (t, J = 7.8 Hz, 4H), 7.35 (d, J = 7.1 Hz, 1H), 7.30 – 7.24 (m, 10H), 6.19 (t, J = 7.3 Hz, 1H), 3.22 (d, J = 7.3 Hz, 2H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 143.4, 142.2, 139.3, 131.7, 130.0, 128.5, 128.34, 128.29, 127.8, 127.6, 127.54, 127.48, 123.9, 123.5, 88.3, 81.1, 20.8.

**HRMS (EI-MS):** calculated $C_{23}H_{18}$: 294.1409, found: 294.1412.

# 4. Mechanism Studies

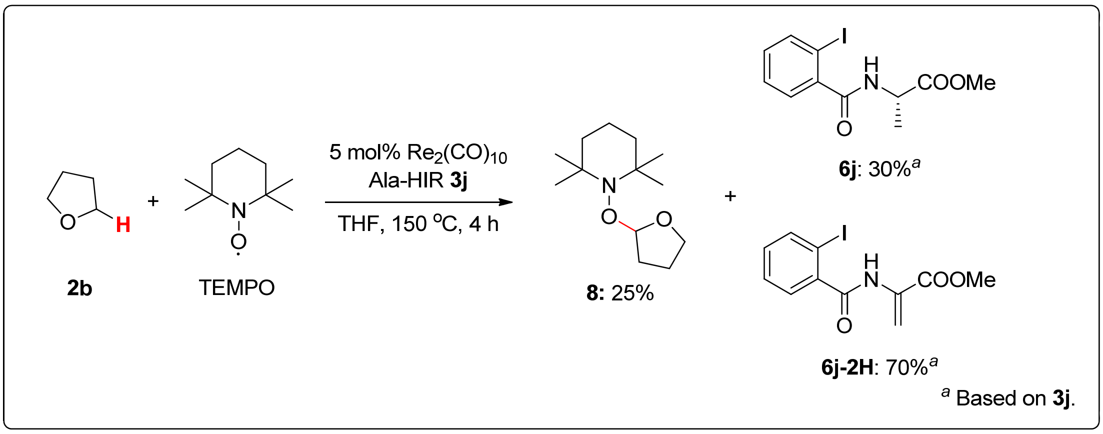
## 4.1 Trapping the C-Radical Formed via H-Abstraction



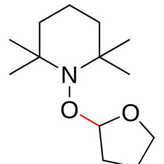
To probe the radical nature of the initial C-H activation step, the radical-trapping reagent TEMPO was subjected to the reaction conditions of olefin **1n** and tetrahydrofuran **2b**. Gratifyingly, the dehydrogenative olefination reaction was completely prohibited and the α-THF radical trapped product **8** was isolated in 31% yield. Meanwhile, methyl 2-(2-iodobenzamido)-propanoate **6j** was isolated in 41% yield and its dehydrogenation product, methyl 2-(2-iodobenzamido)acrylate **6j-2H**, was also isolated in 56% yield, which might originate from the oxidation of **6j** by TEMPO in the reaction.

*Experimental Details:* $Re_2(CO)_{10}$ (32.8 mg, 0.05 mmol, 5 mol%) was added into an oven-dried reaction vessel with Teflon screw cap under nitrogen atmosphere. Then, hypervalent iodine(III) reagent **3j** (1.56 g, 4.0 mmol, 4.0 eq.), TEMPO (124.8mg, 0.8 mmol, 4.0 eq), THF **2b** (30 mL, 0.033 M) and ethene-1,1-diyldibenzene **1n** (180 mg, 1 mmol, 1.0 eq.) were subjected in sequence to the reaction tube. The reaction mixture was stirred in an oil bath at 150 °C for 4 h. Then the reaction mixture was cooled down to room temperature, diluted with $CH_2Cl_2$ (5 mL), and filtered through a short pad of silica, which was then washed with $CH_2Cl_2$ (30 mL). After the removal of the volatiles in vacuo, the crude mixture was pre-adsorbed on silica gel and purified by flash column chromatography(PE:EA=50:1-5:1). The α-THF radical trapped product

**8** was obtained in 31 % isolated yield, which structure was confirmed by HRMS, $^1$H NMR and $^{13}$C NMR. And its data were in agreement with the literature values.[9] In addition, **6j** and **6j-2H** were isolated in 41% and 56% yields respectively.



Furthermore, compound **8** could be also obtained in 25% isolated yield in the absence of **1n** under otherwise the same conditions. **6j** and **6j-2H** were isolated in 30% and 70% yields respectively.

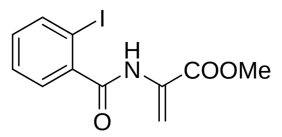


**8**

**$^1$H NMR (300 MHz, CDCl$_3$)** δ 5.41 – 5.32 (m, 1H), 3.94 – 3.74 (m, 2H), 2.07 – 1.86 (m, 3H), 1.86 – 1.70 (m, 1H), 1.48 (s, 5H), 1.38 – 1.16 (m, 4H), 1.15 – 0.95 (m, 9H).

**$^{13}$C NMR (75 MHz, CDCl$_3$)** δ 109.8, 66.8, 60.3, 58.8, 40.2, 39.8, 34.0, 33.5, 31.4, 24.0, 20.6, 20.2, 17.4.

**HRMS (ESI-MS):** calculated $C_{13}H_{26}O_2N^+$ ([M+H]$^+$): 228.19581, found: 228.19617.



**6j-2H**

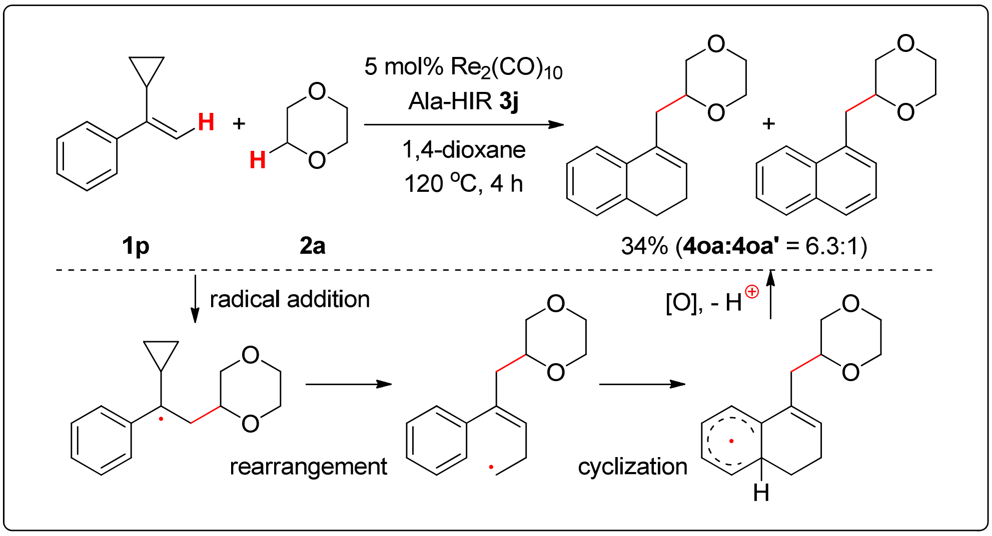
**m.p.:** 101-102 ºC.

**$^1$H NMR (300 MHz, CDCl$_3$)** δ 8.11 (s, 1H), 7.89 (d, J = 7.9 Hz, 1H), 7.49 – 7.35 (m, 2H), 7.13 (td, J = 7.9, 2.1 Hz, 1H), 6.79 (s, 1H), 6.02 (s, 1H), 3.84 (s, 3H).

**$^{13}$C NMR (75 MHz, CDCl$_3$)** δ 167.5, 164.2, 141.4, 140.1, 131.6, 130.8, 128.3, 109.8, 92.3, 53.1.

**HRMS (ESI-MS):** calculated $C_{11}H_{10}O_3NINa^+$ ([M+Na]$^+$): 353.95976, found: 353.96046.

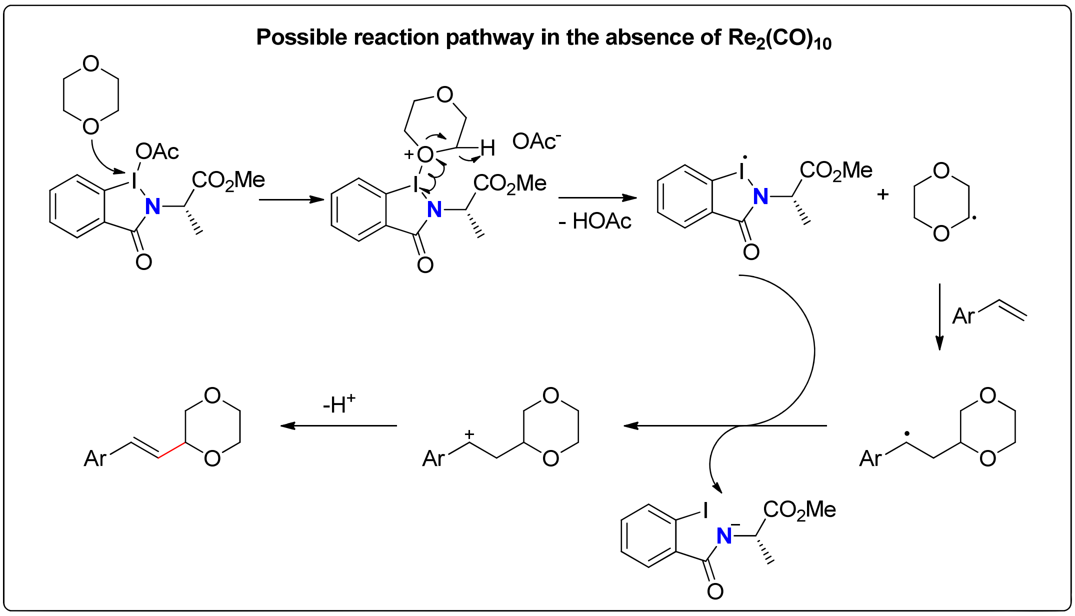
### 4.2 Reaction of 1-phenylvinylcyclopropane with 1,4-dioxane



1-Phenylvinylcyclopropane **1p** is known to participate in radical rearrangements.[10] Therefore, the reaction of **1p** and 1,4-dioxane **2a** in the presence of hypervalent iodine(III) reagent **3j** was conducted, which gave the ring expansion product **4oa** and its aromatized product **4oa'** in 34 % combined yield with a ratio of 6.3:1, supporting a reaction sequence of radical addition/rearrangement/cyclization/oxidative deprotonation.[10]

*Experimental Details:* $Re_2(CO)_{10}$ (3.26 mg, 0.005 mmol, 2.5 mol%) was added into an oven-dried reaction vessel with Teflon screw cap under nitrogen atmosphere. Then, hypervalent iodine(III) reagent **3j** (312 mg, 0.8 mmol, 4.0 eq.), 1,4-dioxane (4 mL, 0.05 M) and 1-phenylvinylcyclopropane **1p** (28.8 mg, 0.2 mmol, 1.0 eq.) were subjected in sequence to the reaction tube. The reaction mixture was stirred in an oil bath at 120 °C for 4 h. Then the reaction mixture was cooled down to room temperature, diluted with $CH_2Cl_2$ (5 mL), and filtered through a short pad of silica, which was then washed with $CH_2Cl_2$ (30 mL). After the removal of the volatiles in vacuo, the crude mixture was pre-adsorbed on silica gel and purified by flash column chromatography (EA : PE = 1:10) to afford the mixed product **4oa** and **4oa'** in 34 % combined yield (**4oa**:**4oa'** = 6.3:1) as a colorless oil. The ratio of the two products was identified by GC-MS.

In addition, we think the mechanism of the radical generation step in the absence of $Re_2(CO)_{10}$ is different from that in the presence of the rhenium catalyst. As shown below, 1,4-dioxane itself acts as a reductant and is oxidized by the hypervalent iodine(III) reagent through SET mechanism to give the I-radical and 1,4-dioxane C-radical species. The similar process was also found for the formation of C-radical species of THF by using iodobenzene diacetate (Kim, Y.; Ahn, K. *Synth. Commun.* **1999**, *29*, 4361). Afterwards, the I-radical species further oxidized the key benzylic radical intermediate to give the olefination product after elimination of a proton. As a whole, the hypervalent iodine(III) reagent itself can participate in the oxidative olefination of 1,4-dioxane in the absence of the rhenium catalyst. However, this process is relatively more difficult in comparison with the Re-catalyzed pathway.



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5. Zhdankin, V. V.; Arbit, R. M.; Lynch, B. J.; Kiprof, P. *J. Org. Chem.* **1998**, *63*, 6590.
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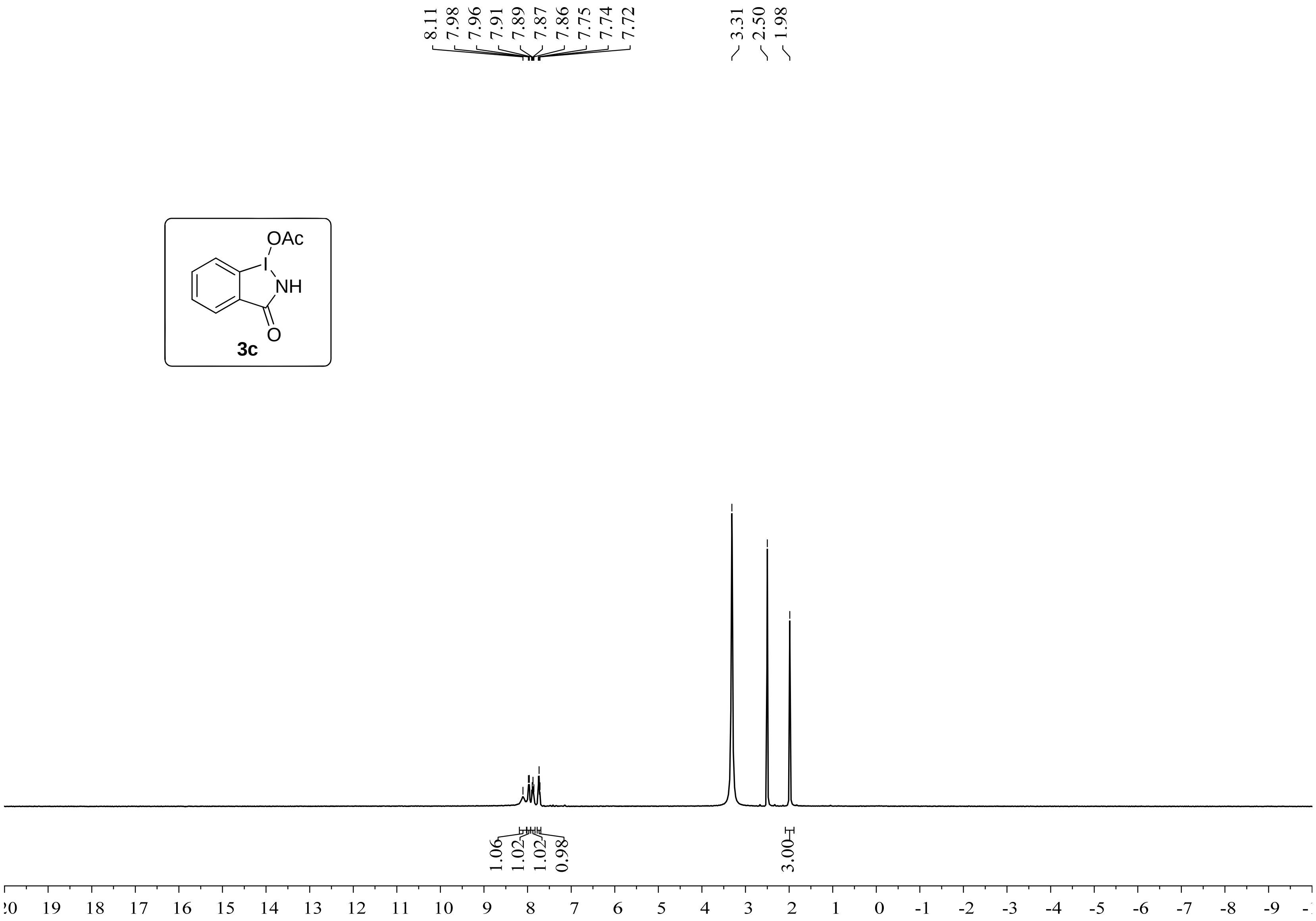
9. Pan, S.; Liu, J.; Li, H.; Wang, Z.; Guo, X.; Li, Z. *Org. Lett.*, **2010**, *12*, 1932
10. Liwosz, T. W.; Chemler, S. R. *Org. Lett.* **2013**, *15*, 3034.

## 6. $^{1}$H NMR and $^{13}$C NMR Spectra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7.89
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7.75
7.74
7.72
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1.98
OAc
I
NH
O
3c
1.06
1.02
1.02
0.98
3.00
19
18
17
16
15
14
13
12
11
10
9
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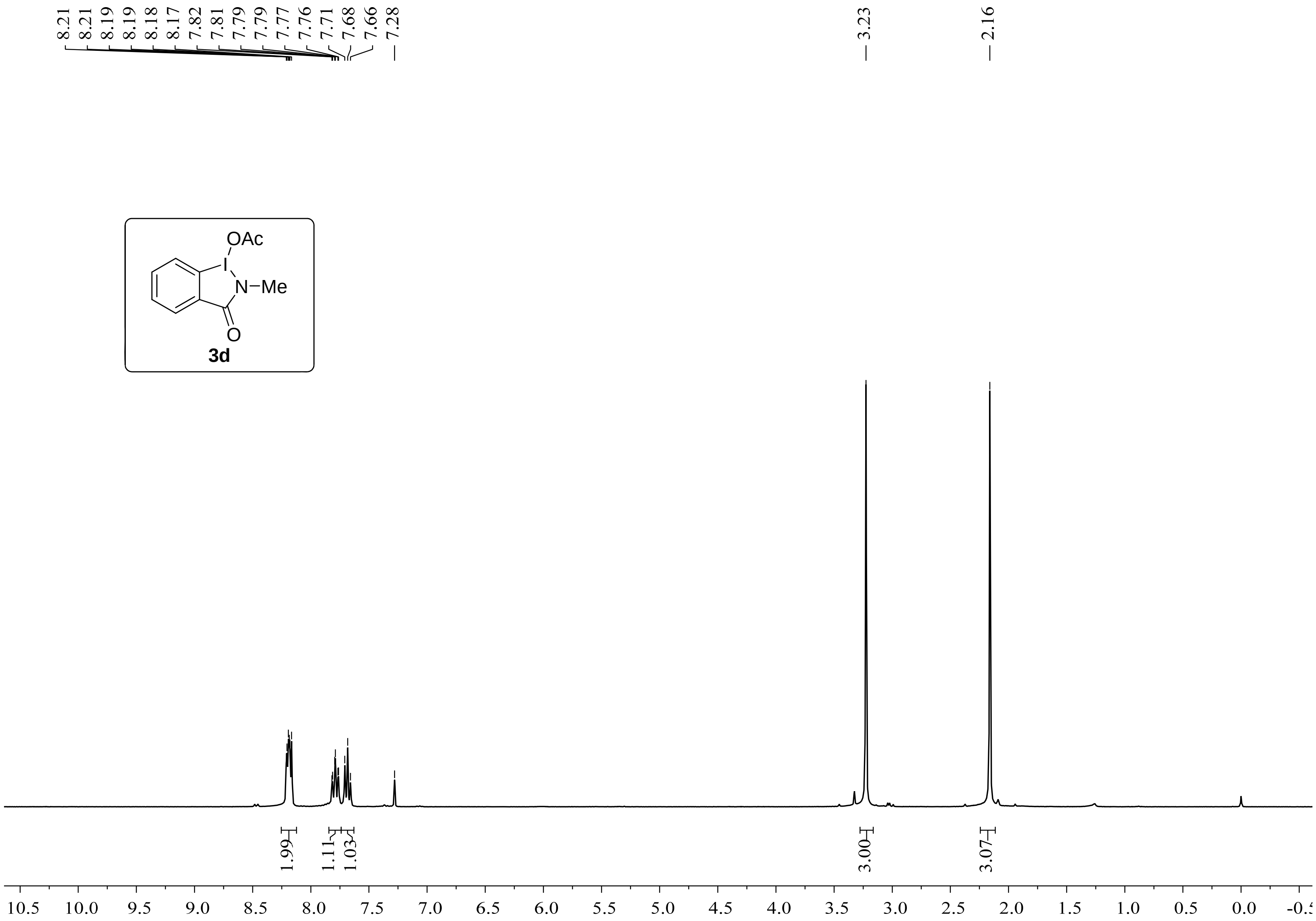
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7.68
7.66
7.28
3.23
2.16
OAc
I
N−Me
O
3d
1.99
1.11
1.03
3.00
3.07
10.5
10.0
9.5
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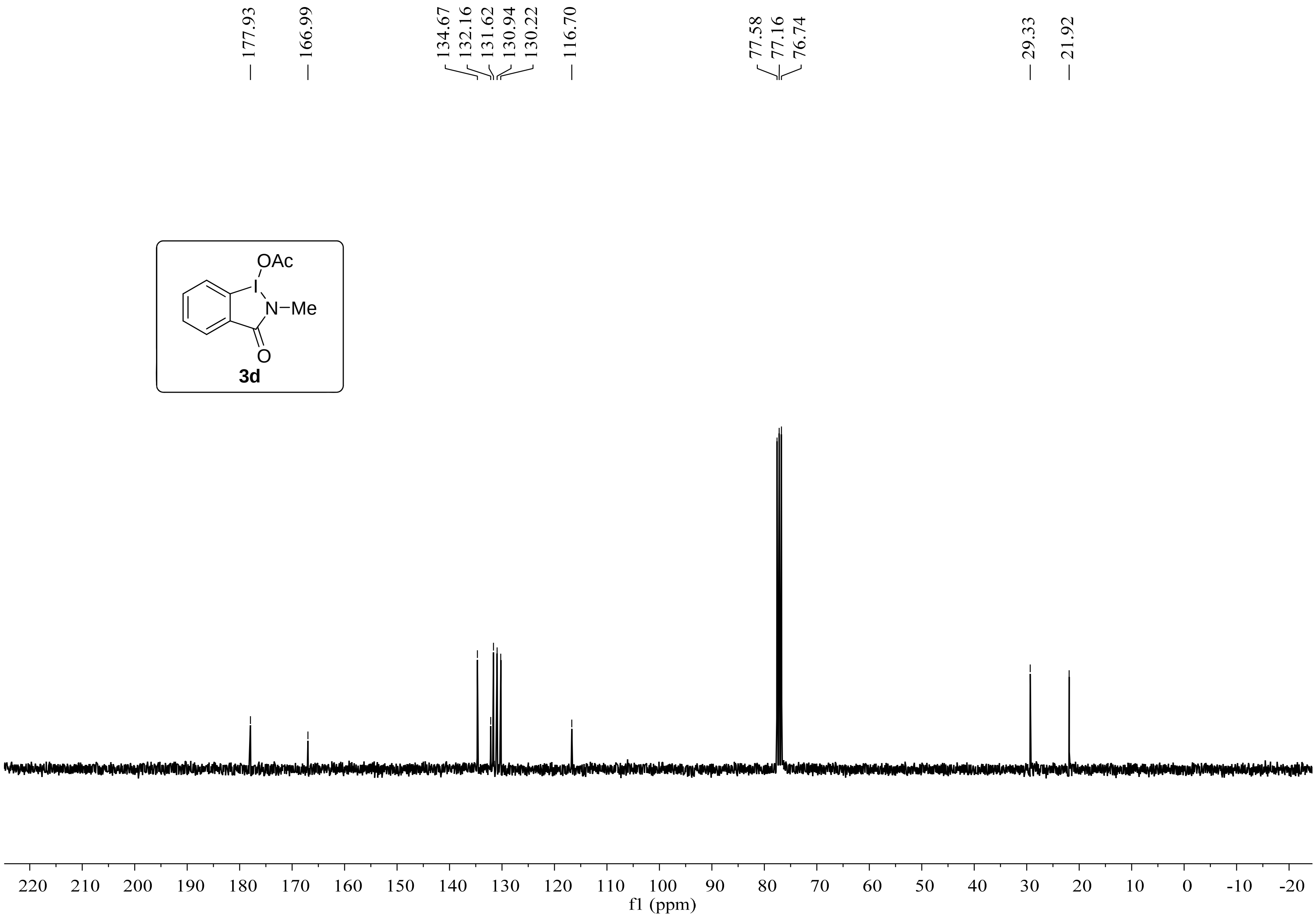
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OAc
I
N−Me
O
3d
220
210
200
190
180
170
160
150
140
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100
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50
40
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20
10
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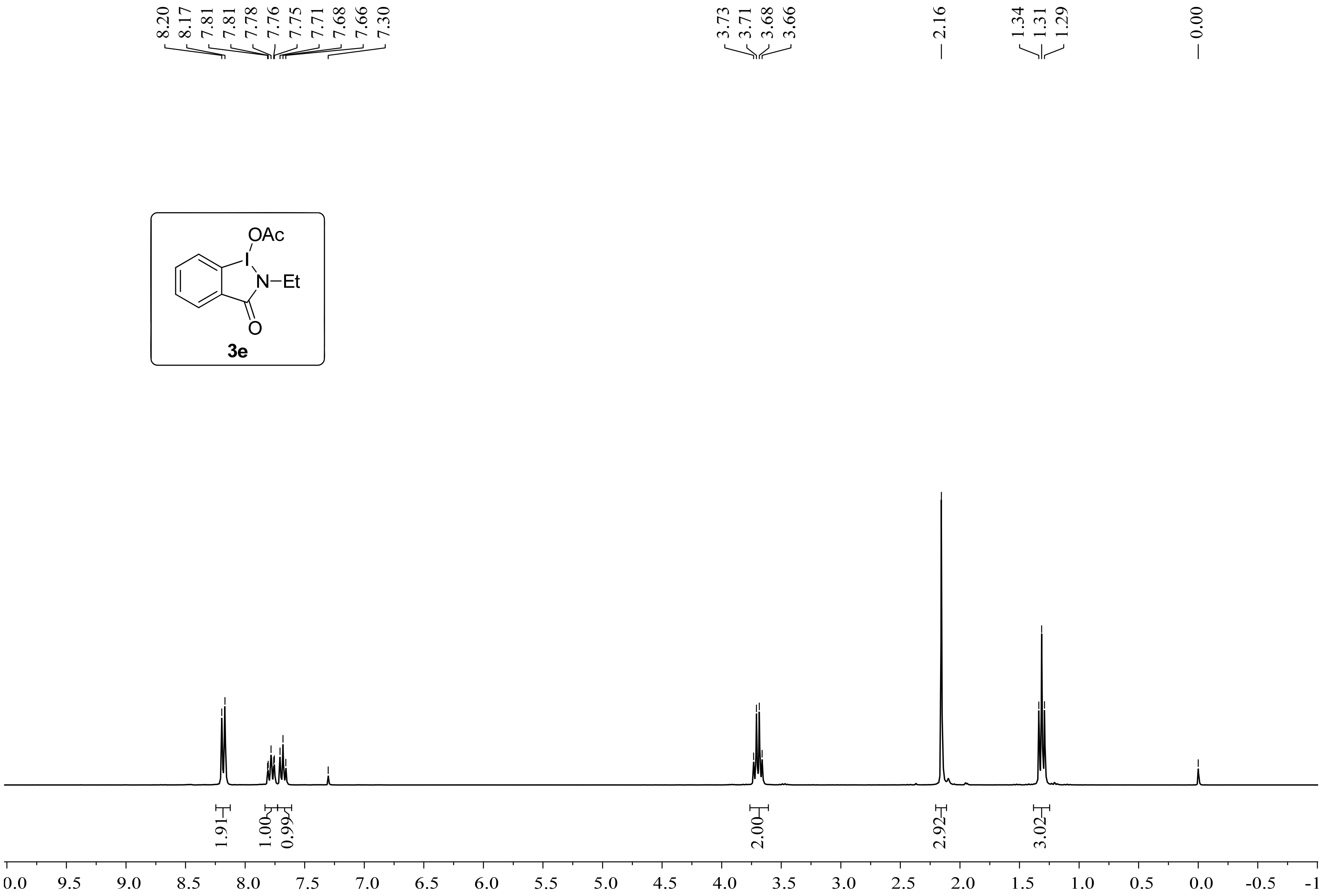
-20
f1 (ppm)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3.66
2.16
1.34
1.31
1.29
0.00
OAc
I
N–Et
O
3e
1.91
1.00
0.99
2.00
2.92
3.02
0.0
9.5
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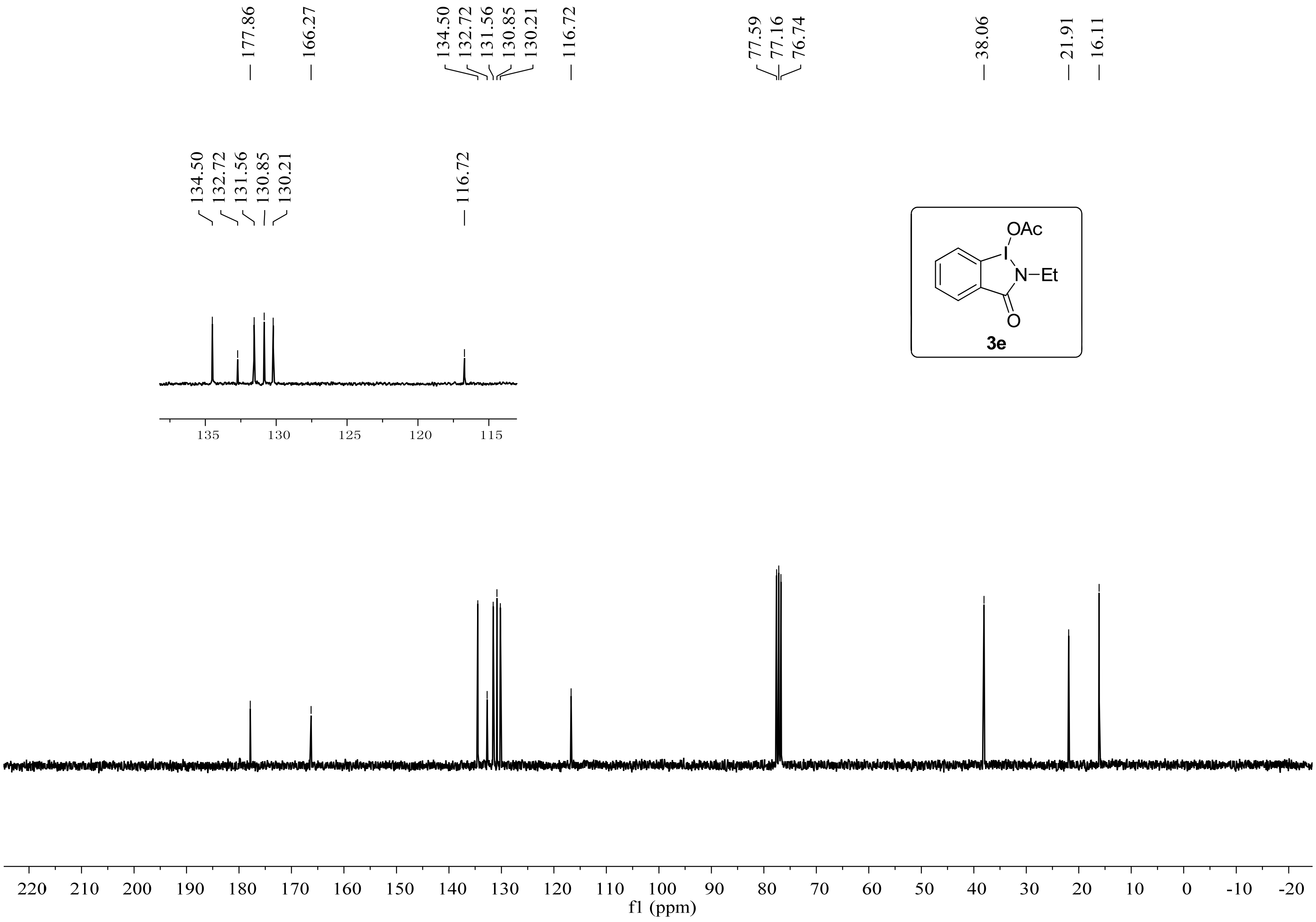
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16.11
135
130
125
120
115
OAc
I
N−Et
O
3e
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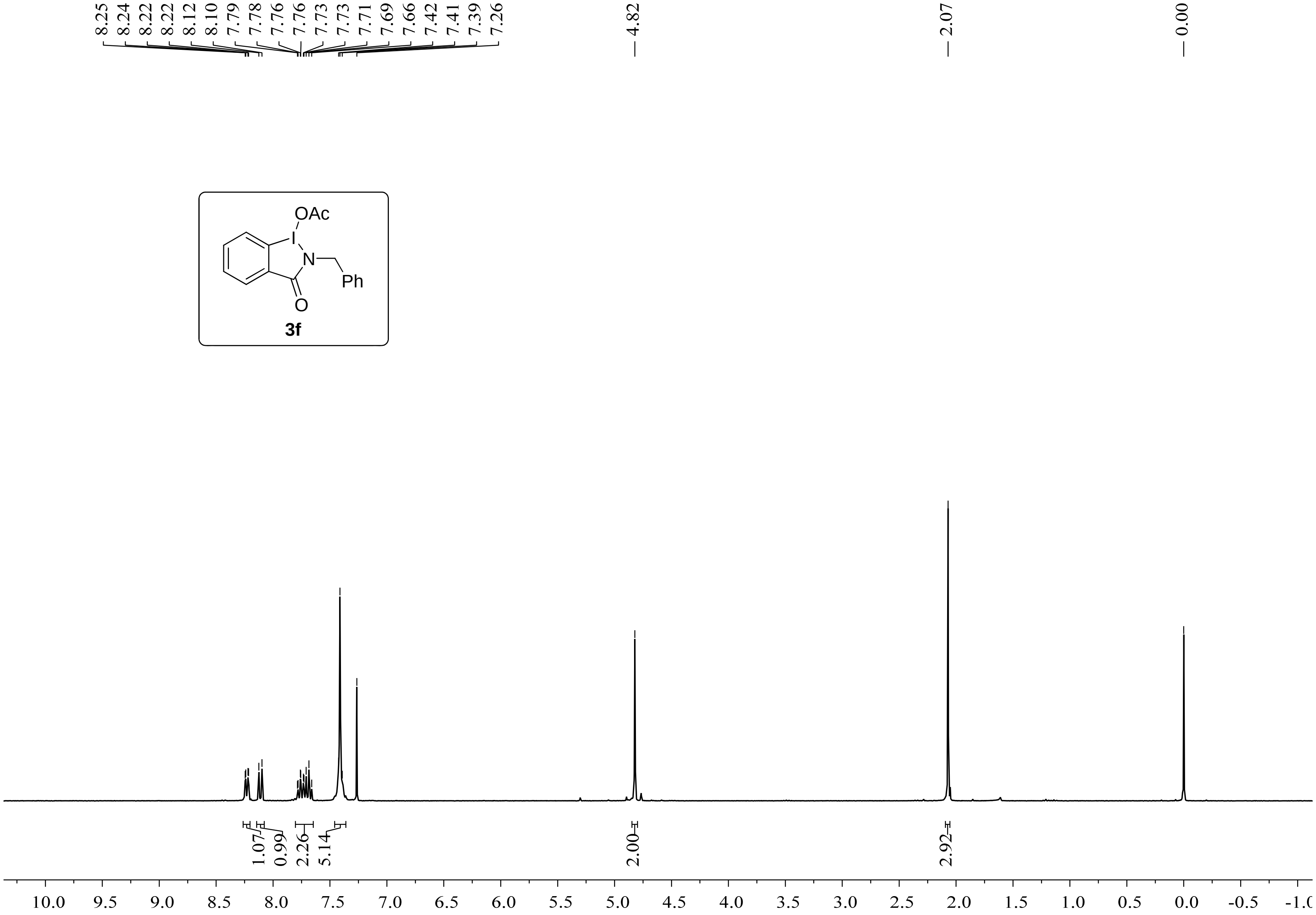
f1 (ppm)

OAc
I
N
Ph
O

**3f**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7.71
7.69
7.66
7.42
7.41
7.39
7.26
4.82
2.07
0.00
1.07
0.99
2.26
5.14
2.00
2.92
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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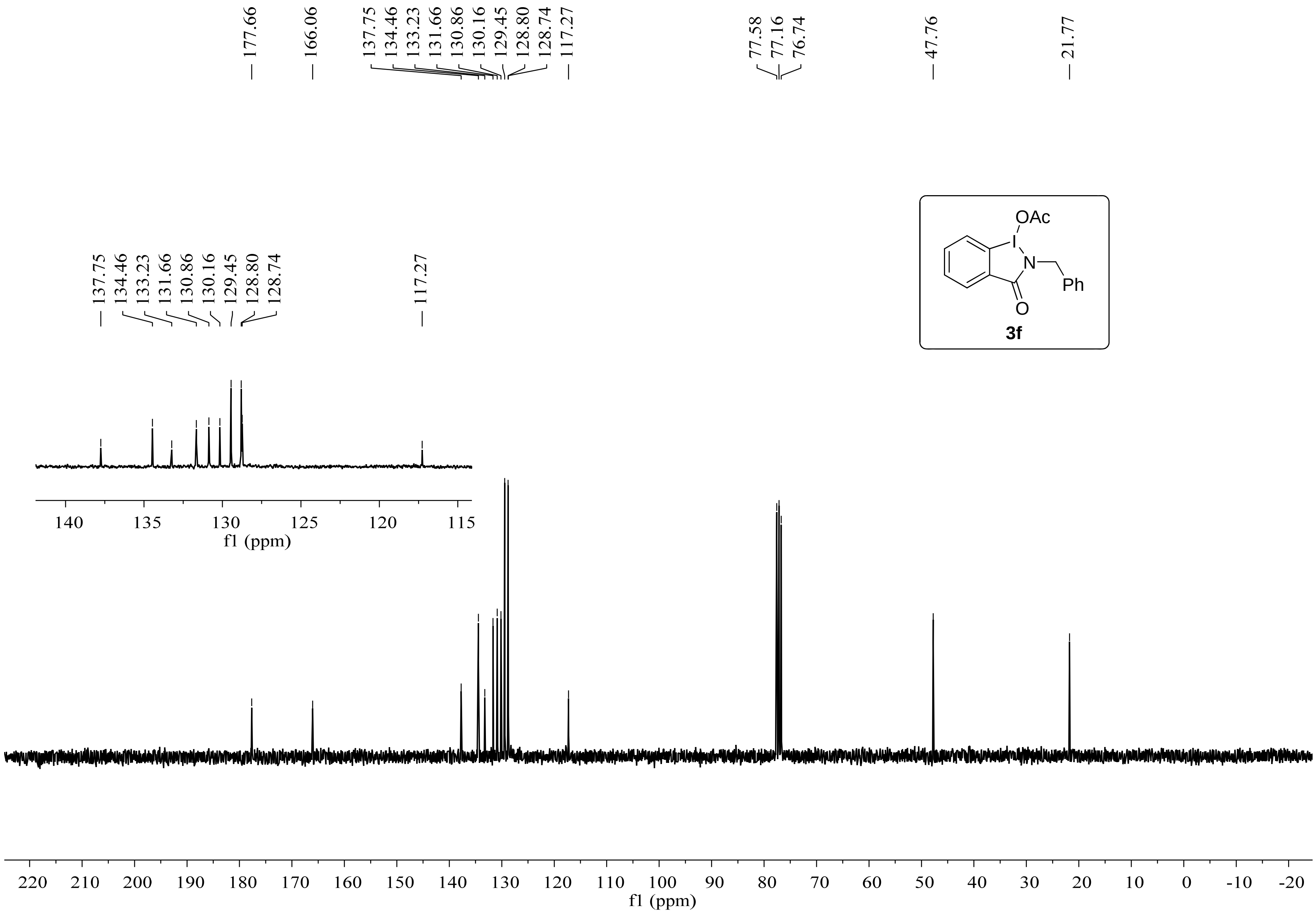
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77.16
76.74
47.76
21.77
140
135
130
125
120
115
f1 (ppm)
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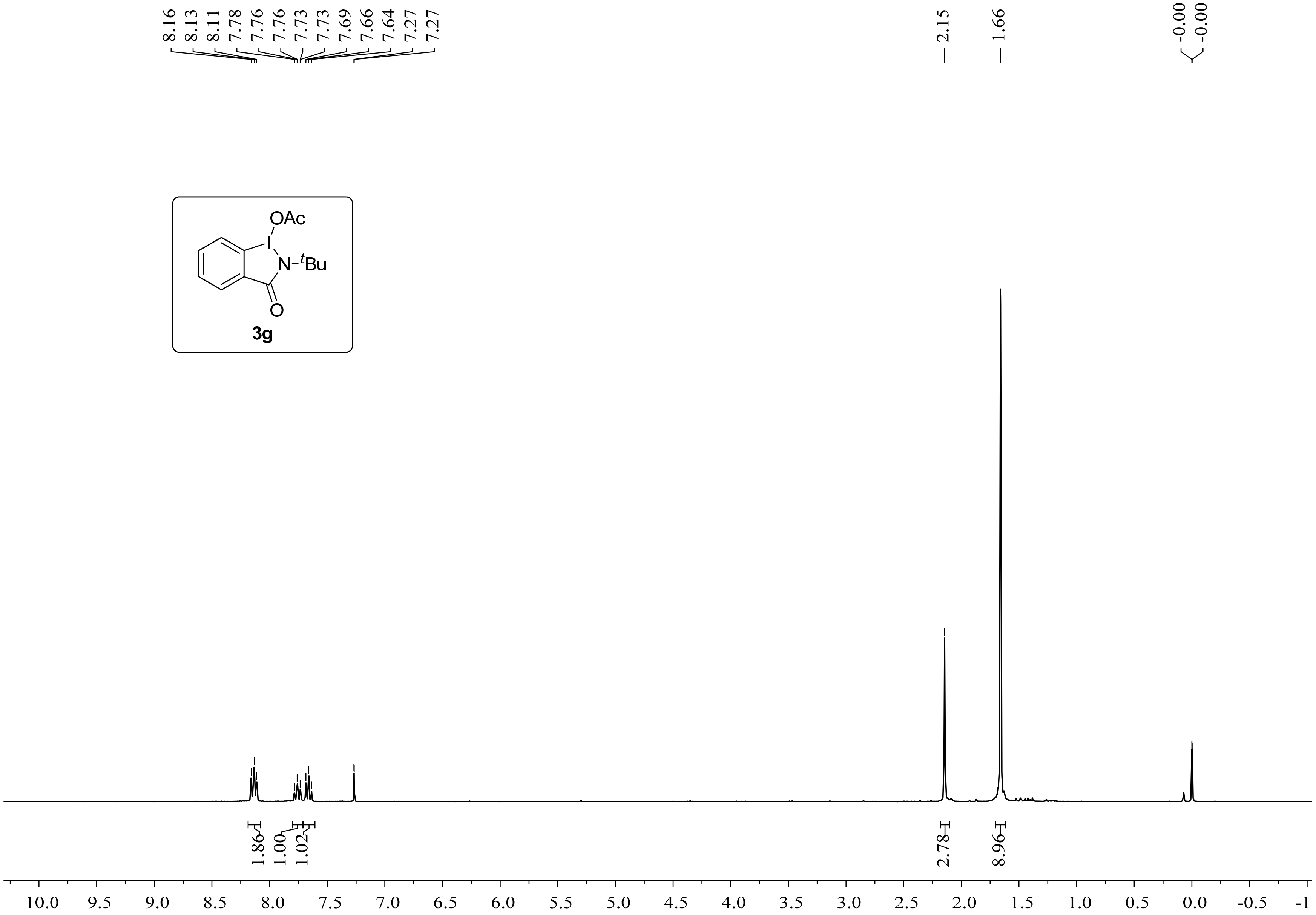
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

OAc
I
N
Ph
O

**3f**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8.13
8.11
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7.76
7.76
7.73
7.73
7.69
7.66
7.64
7.27
7.27
2.15
1.66
-0.00
-0.00
OAc
I
N-$^t$Bu
O
3g
1.86
1.00
1.02
2.78
8.96
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
2.5
2.0
1.5
1.0
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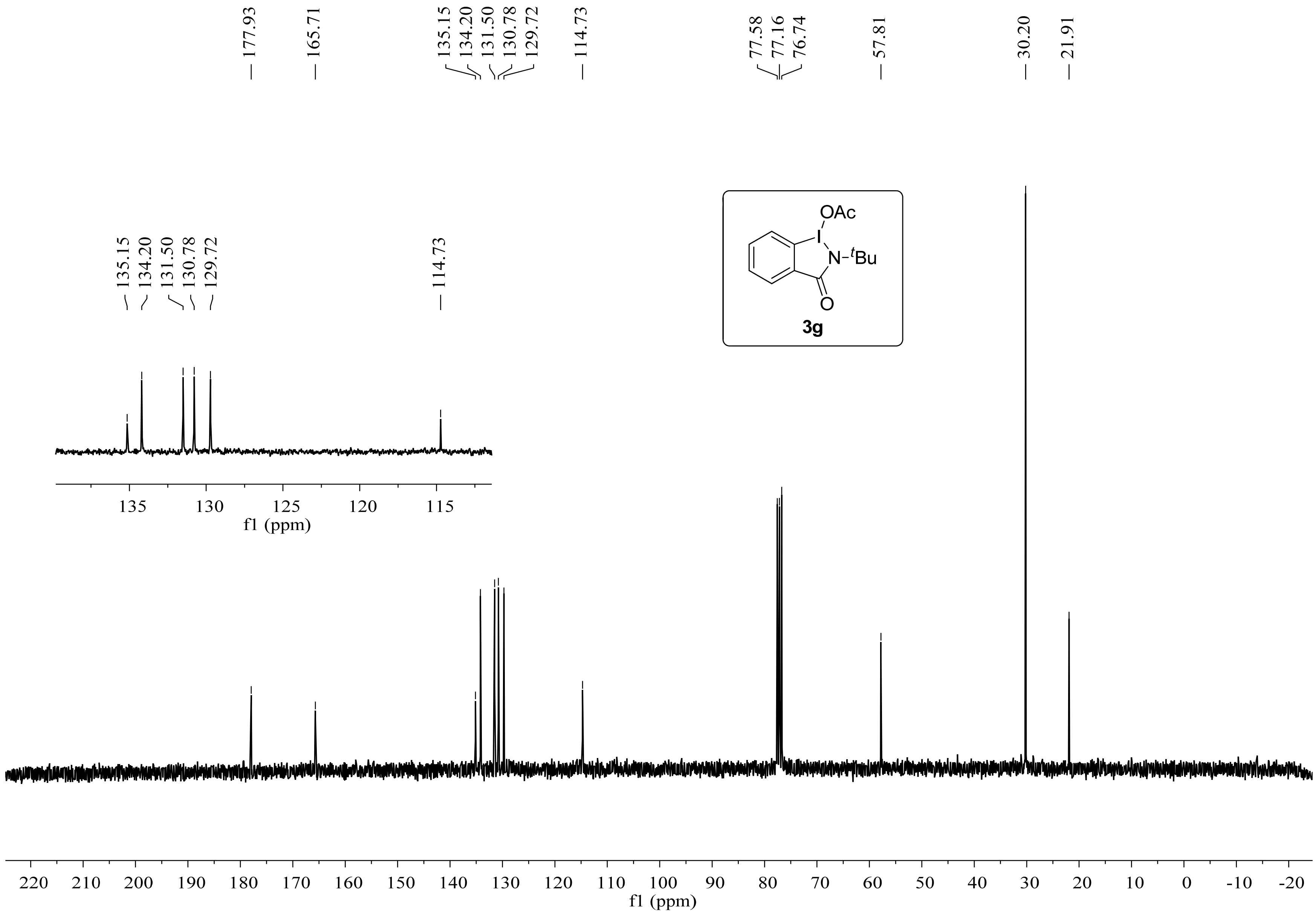
0.0
-0.5
-1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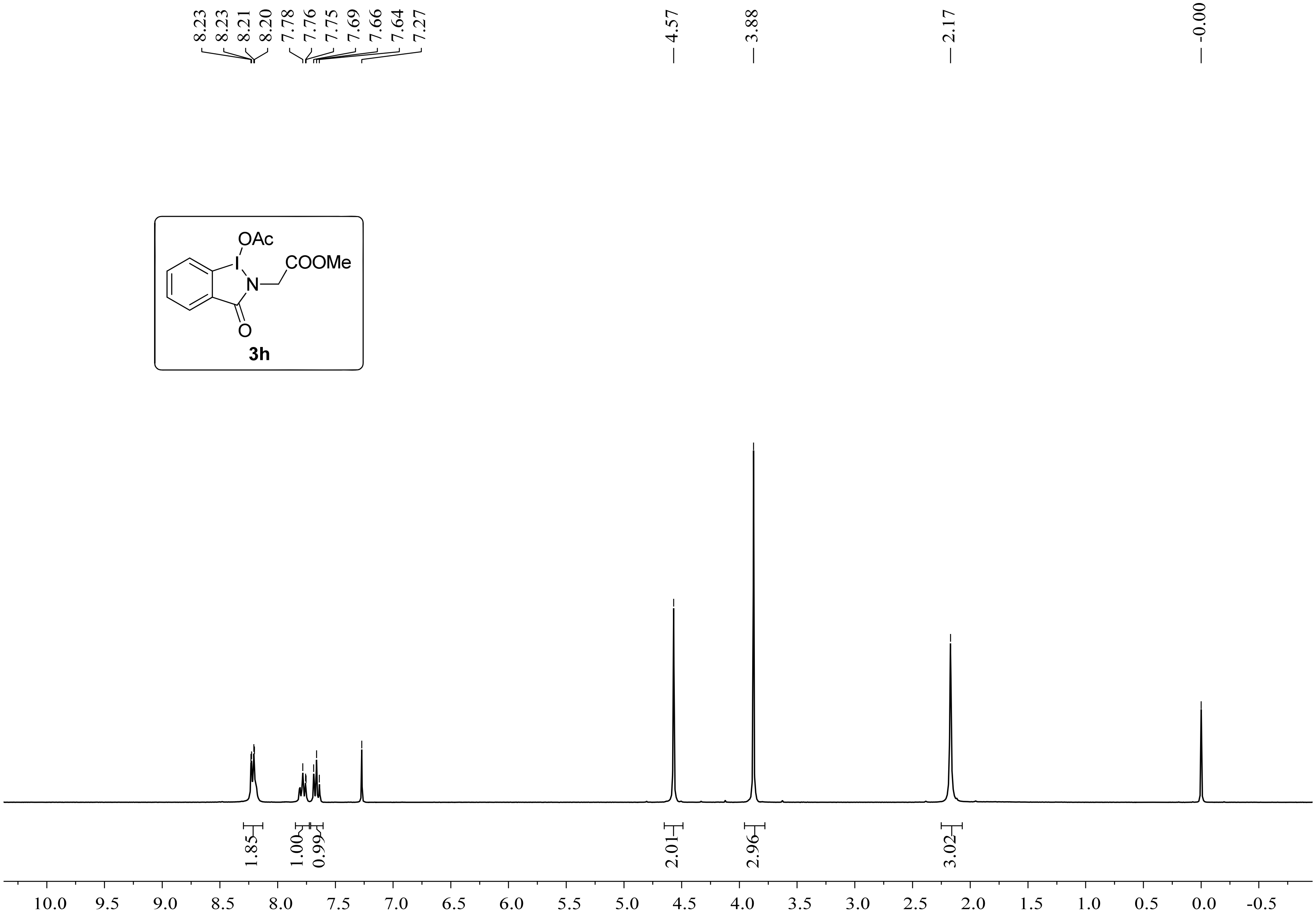
165.71
135.15
134.20
131.50
130.78
129.72
114.73
77.58
77.16
76.74
57.81
30.20
21.91
OAc
I
N-$^t$Bu
O
3g
135
130
125
120
115
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)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8.23
8.21
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7.78
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7.75
7.69
7.66
7.64
7.27
4.57
3.88
2.17
-0.00
OAc
I
N
COOMe
O
3h
1.85
1.00
0.99
2.01
2.96
3.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.5
3.0
2.5
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0.0
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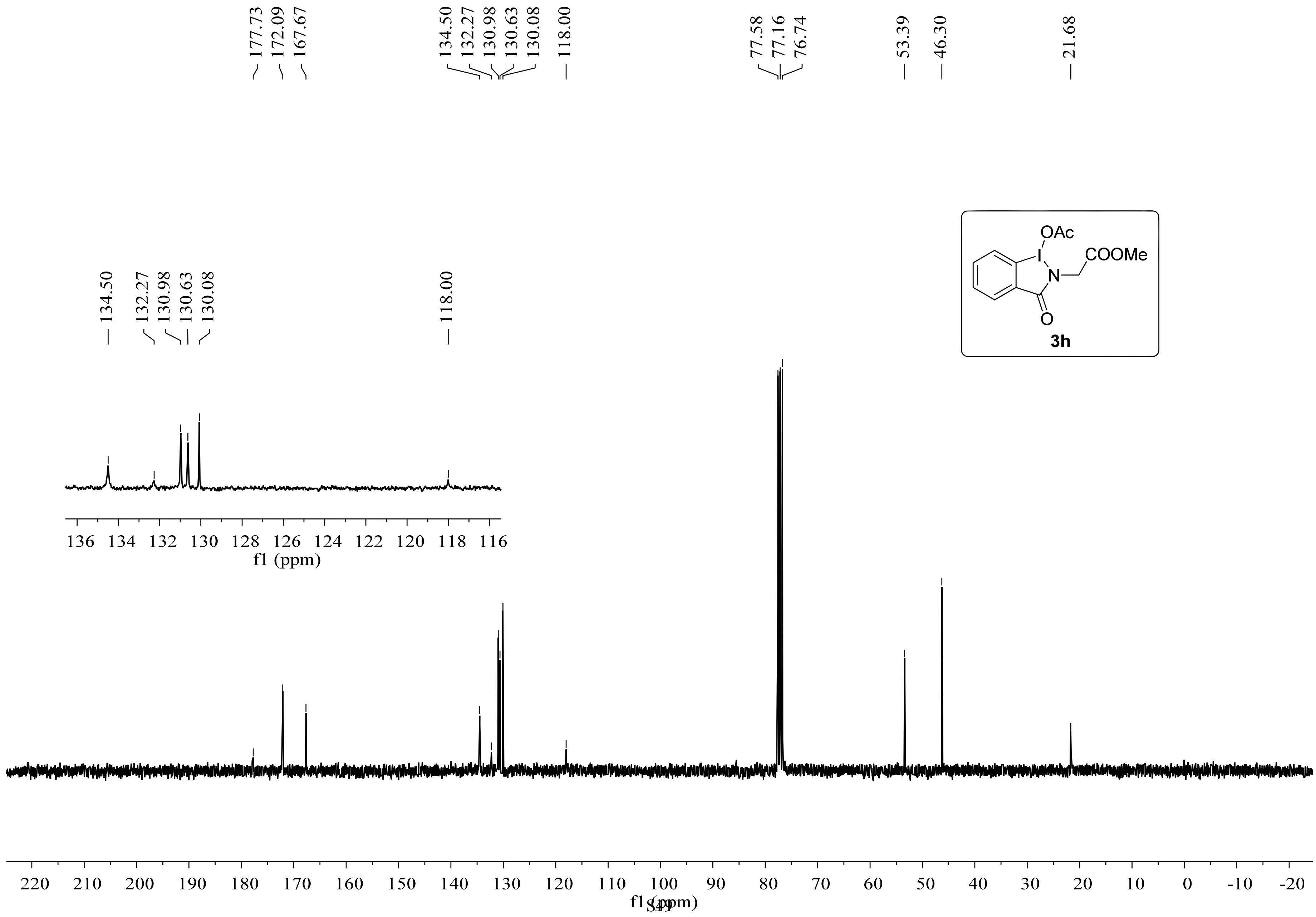
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130.63
130.08
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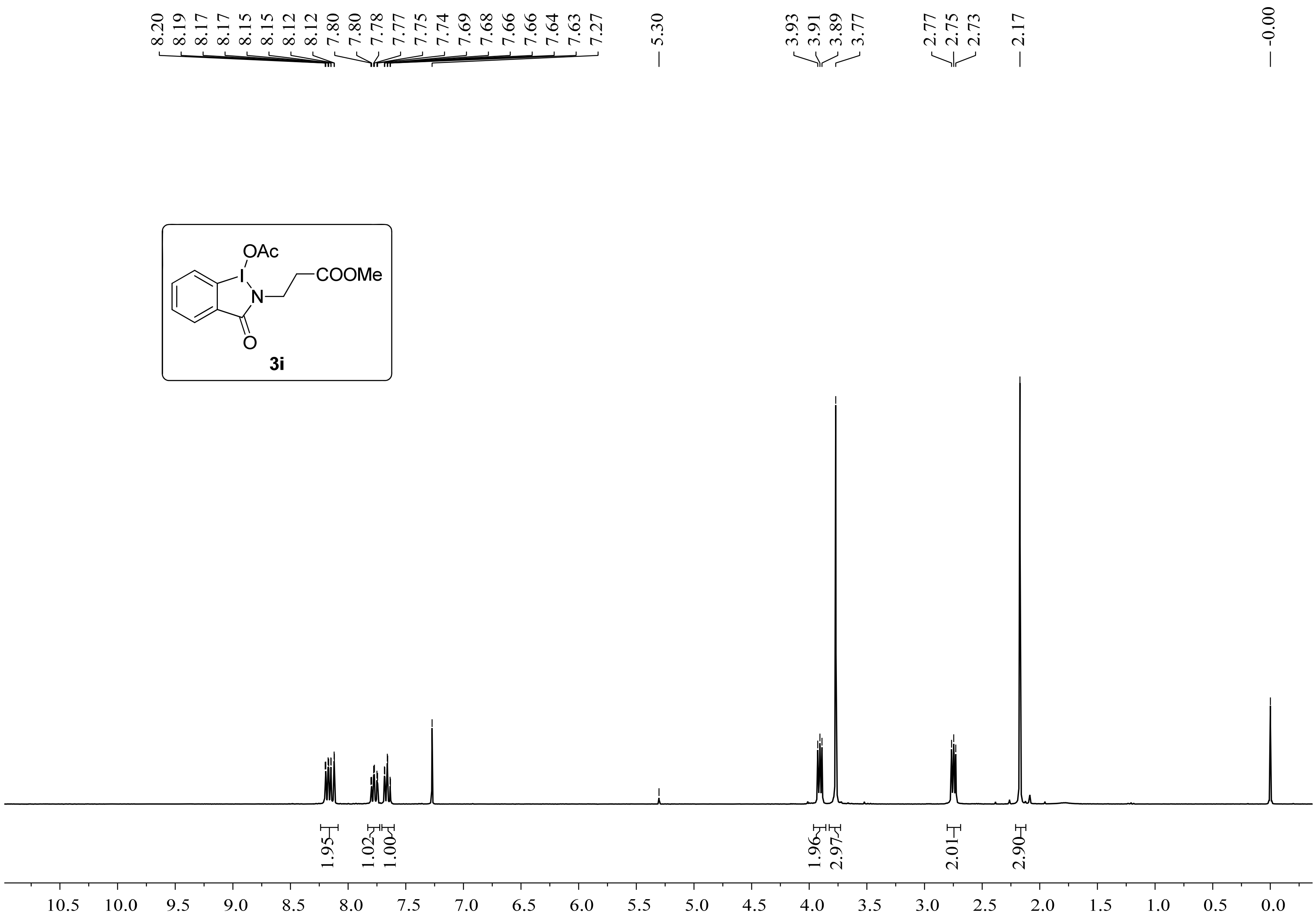
77.58
77.16
76.74
53.39
46.30
21.68
134.50
132.27
130.98
130.63
130.08
118.00
136 134 132 130 128 126 124 122 120 118 116
f1 (ppm)
OAc
I
N
COOMe
O
3h
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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8.12
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7.80
7.78
7.77
7.75
7.74
7.69
7.68
7.66
7.66
7.64
7.63
7.27
5.30
3.93
3.91
3.89
3.77
2.77
2.75
2.73
2.17
-0.00
OAc
I
N
COOMe
O
3i
1.95
1.02
1.00
1.96
2.97
2.01
2.90
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
4.0
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1.0
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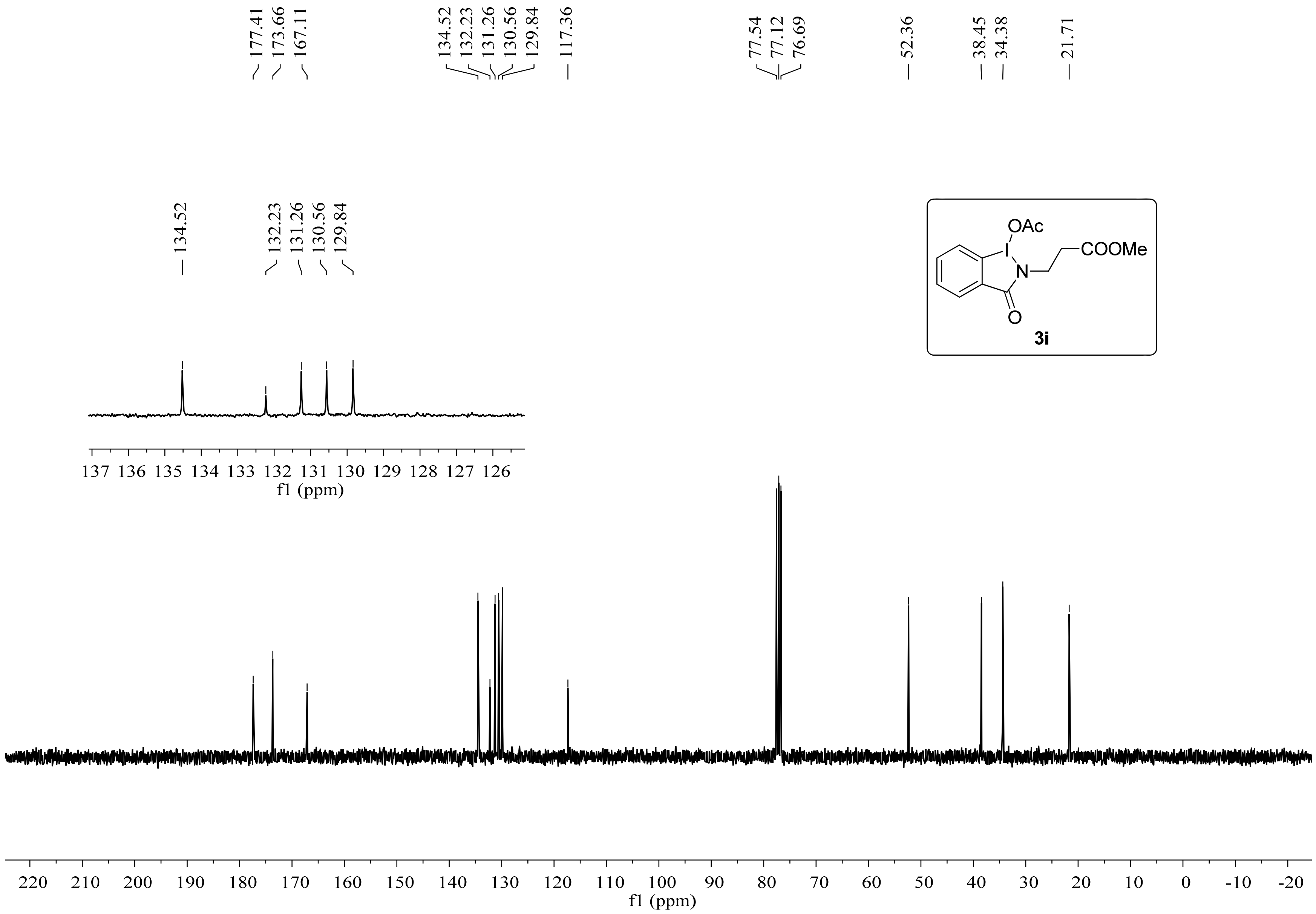
0.0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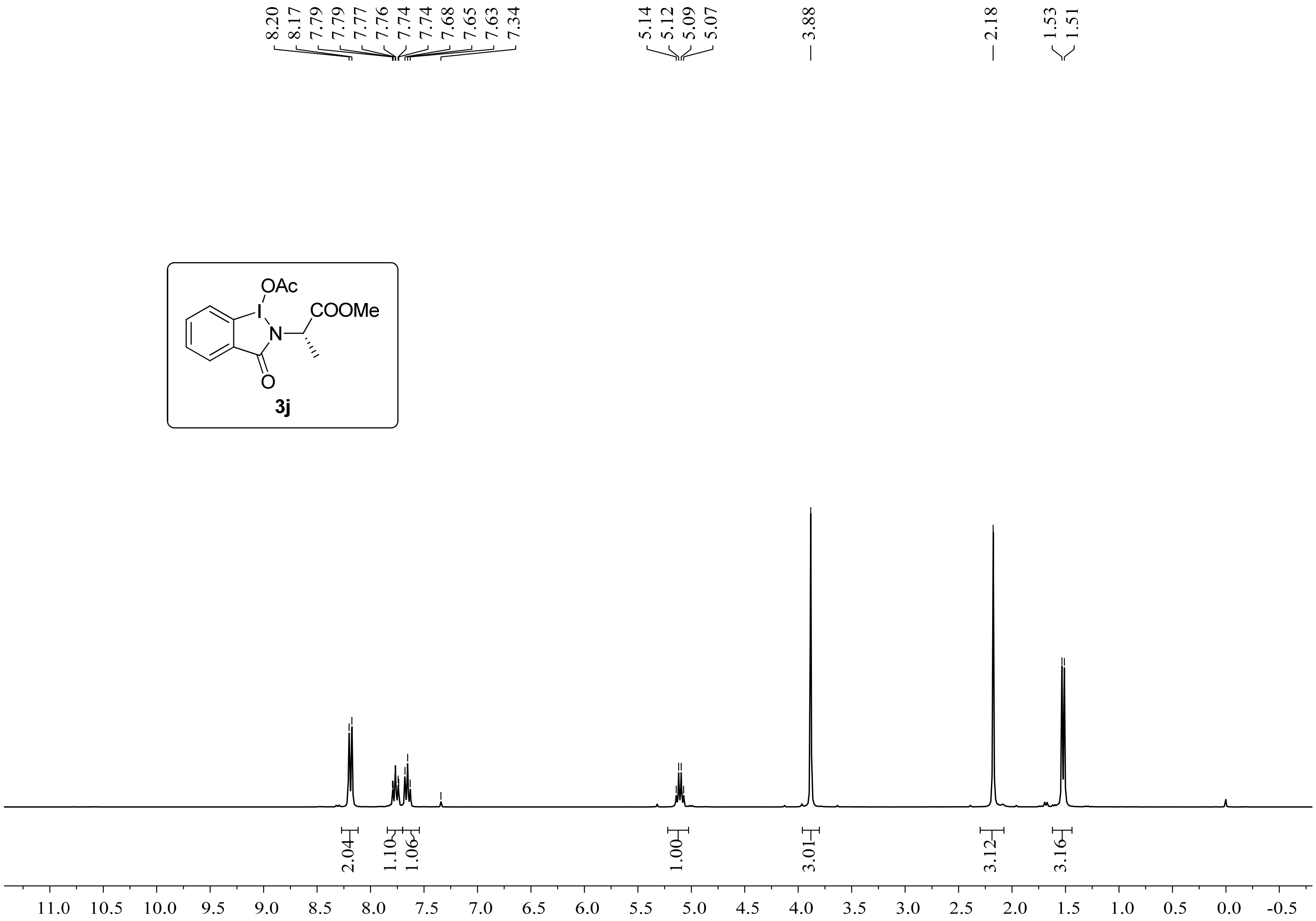
173.66
167.11
134.52
132.23
131.26
130.56
129.84
117.36
77.54
77.12
76.69
52.36
38.45
34.38
21.71
OAc
I
N
COOMe
O
137 136 135 134 133 132 131 130 129 128 127 126
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

**3i**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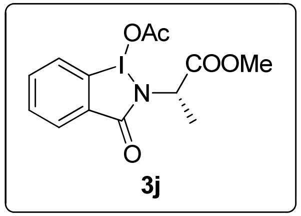
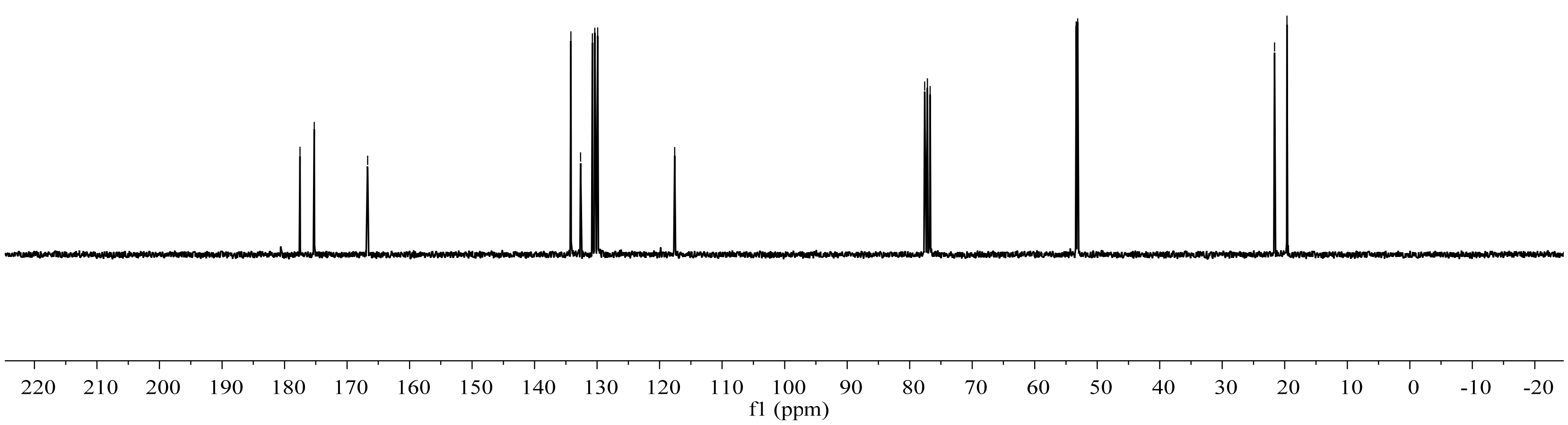
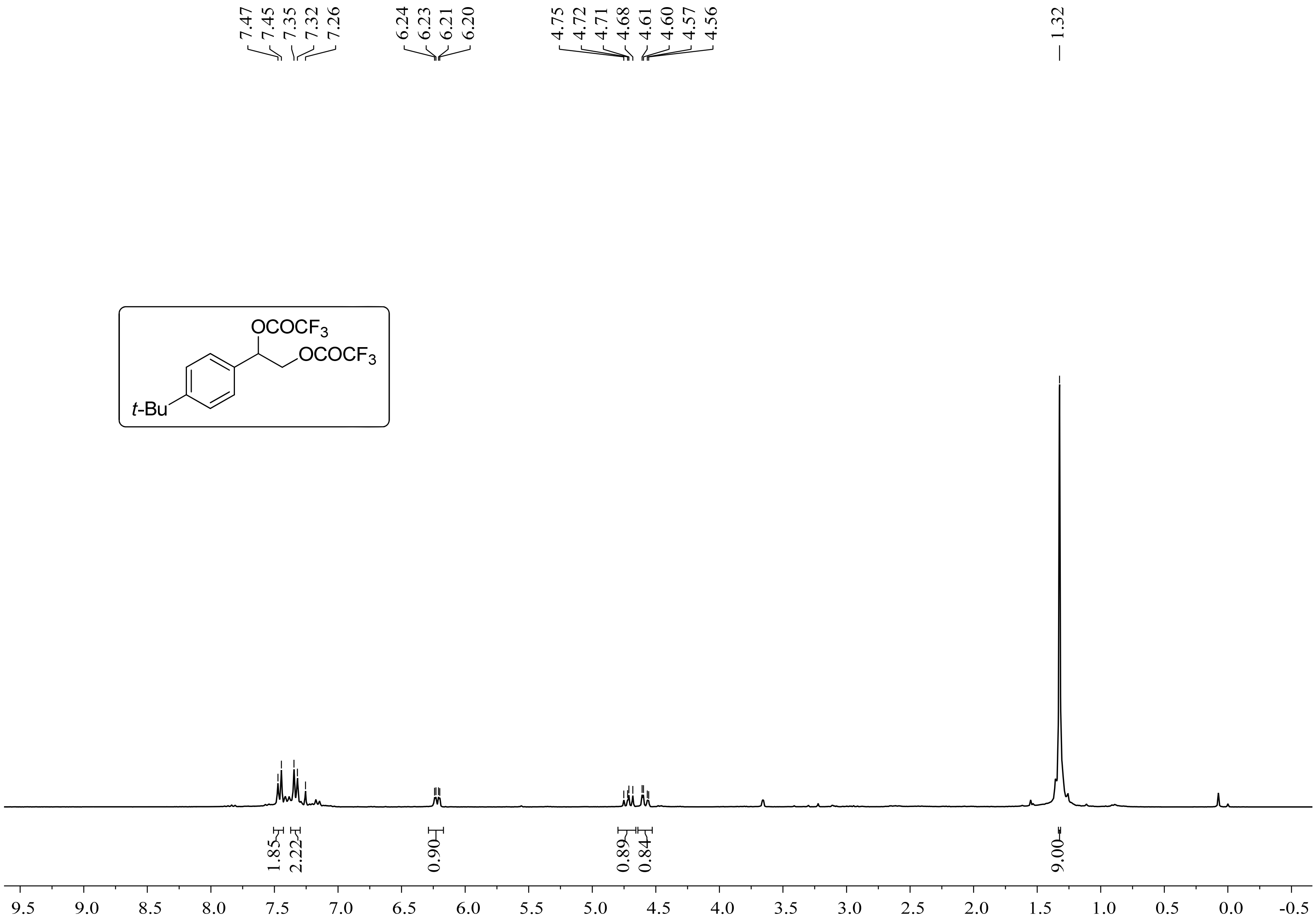
8.17
7.79
7.79
7.77
7.76
7.74
7.74
7.68
7.65
7.63
7.34
5.14
5.12
5.09
5.07
3.88
2.18
1.53
1.51
OAc
I
N
COOMe
O
3j
2.04
1.10
1.06
1.00
3.01
3.12
3.16
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

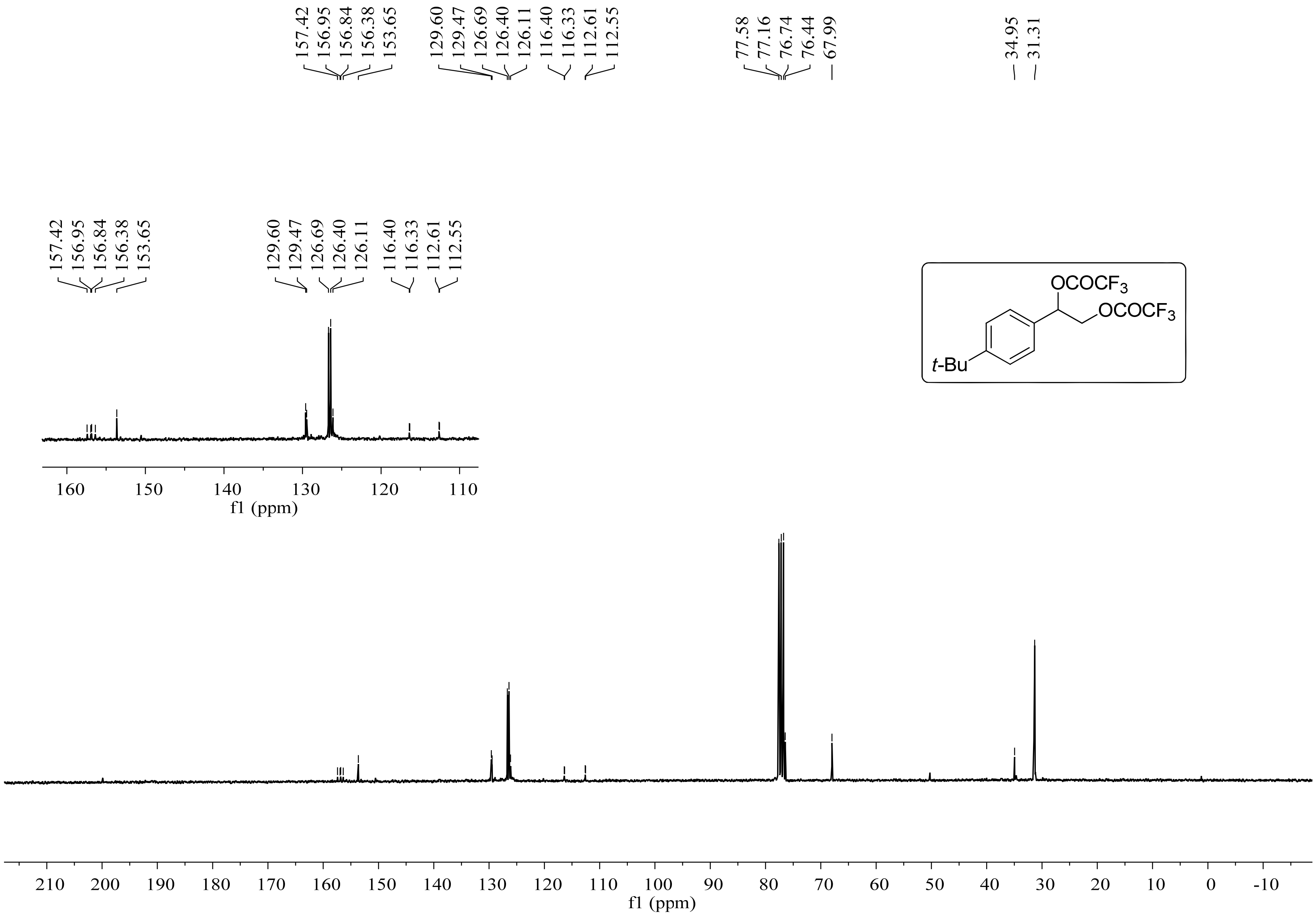


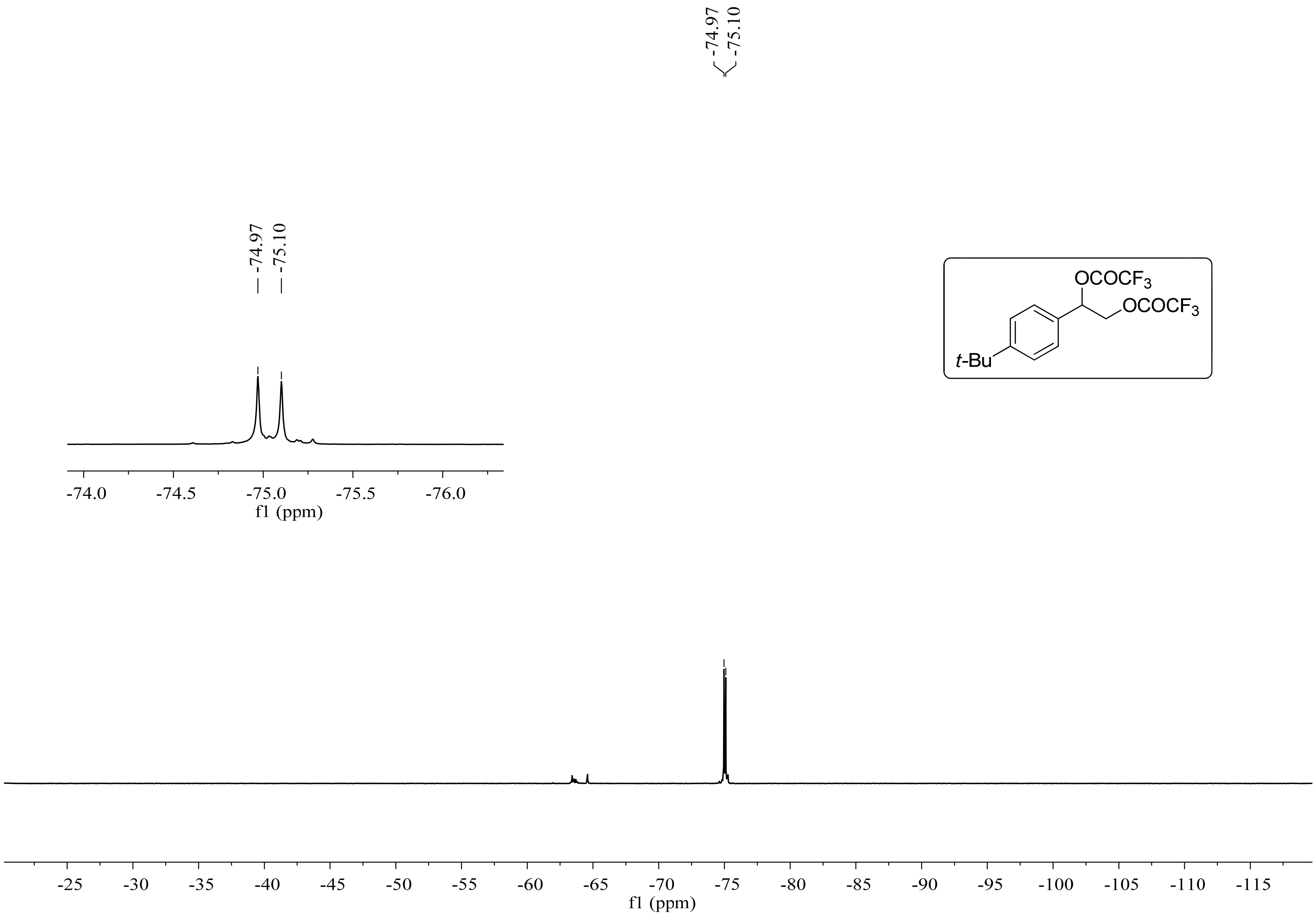
**3j**

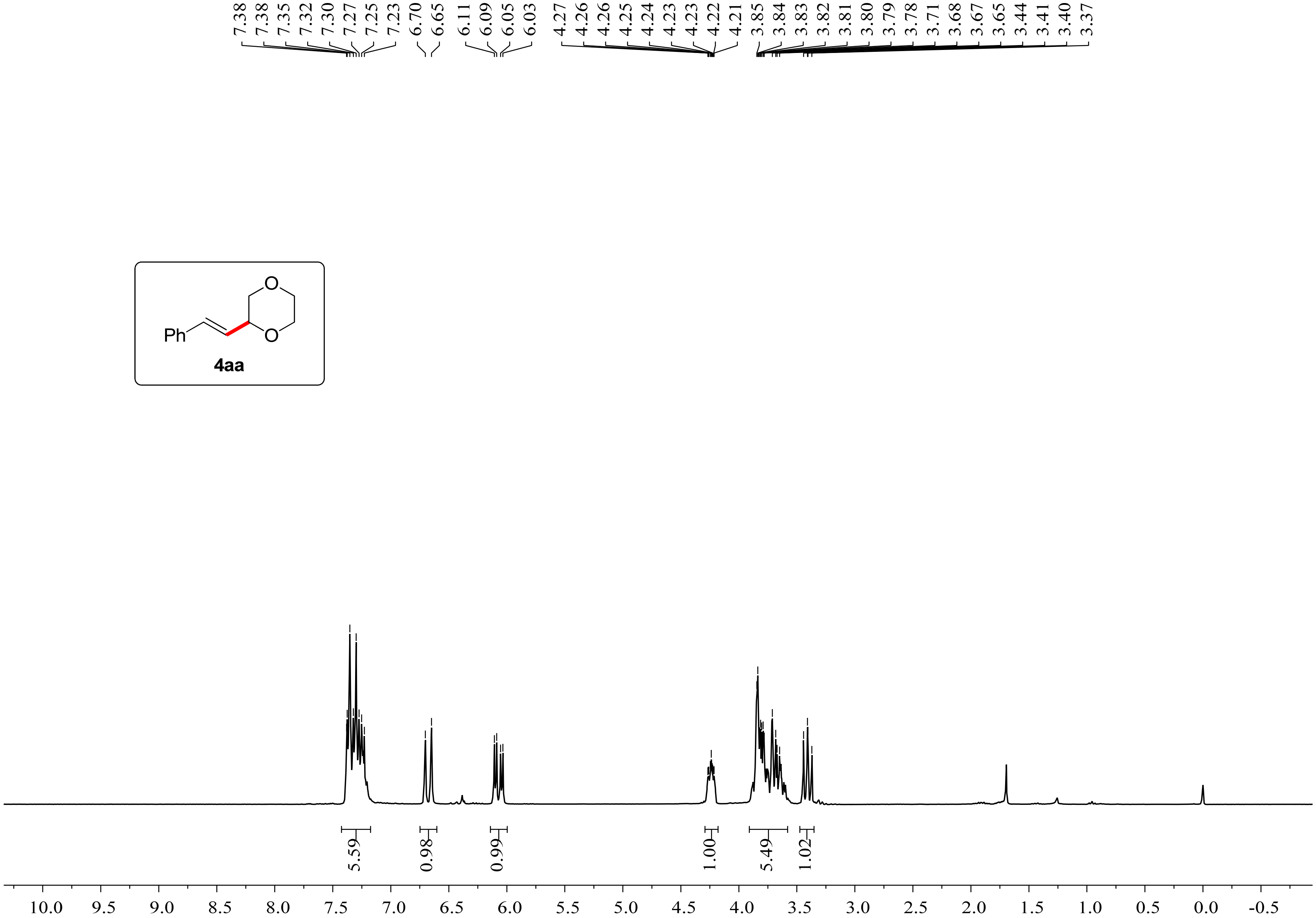


177.53
175.24
166.71
134.20
132.64
130.77
130.37
129.92
117.59
77.59
77.16
76.73
53.36
53.12
21.63
19.65
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


7.47
7.45
7.35
7.32
7.26
6.24
6.23
6.21
6.20
4.75
4.72
4.71
4.68
4.61
4.60
4.57
4.56
1.32
OCOCF3
OCOCF3
t-Bu
1.85
2.22
0.90
0.89
0.84
9.00
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


157.42
156.95
156.84
156.38
153.65
129.60
129.47
126.69
126.40
126.11
116.40
116.33
112.61
112.55
77.58
77.16
76.74
76.44
67.99
34.95
31.31
160
150
140
130
120
110
f1 (ppm)
OCOCF3
OCOCF3
t-Bu
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)


-74.97
-75.10
-74.97
-75.10
-74.0
-74.5
-75.0
-75.5
-76.0
f1 (ppm)
OCOCF3
OCOCF3
t-Bu
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
f1 (ppm)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7.38
7.35
7.32
7.30
7.27
7.25
7.23
6.70
6.65
6.11
6.09
6.05
6.03
4.27
4.26
4.26
4.25
4.24
4.23
4.23
4.22
4.21
3.85
3.84
3.83
3.82
3.81
3.80
3.79
3.78
3.71
3.68
3.67
3.65
3.44
3.41
3.40
3.37
Ph
O
O
4aa
5.59
0.98
0.99
1.00
5.49
1.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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3.5
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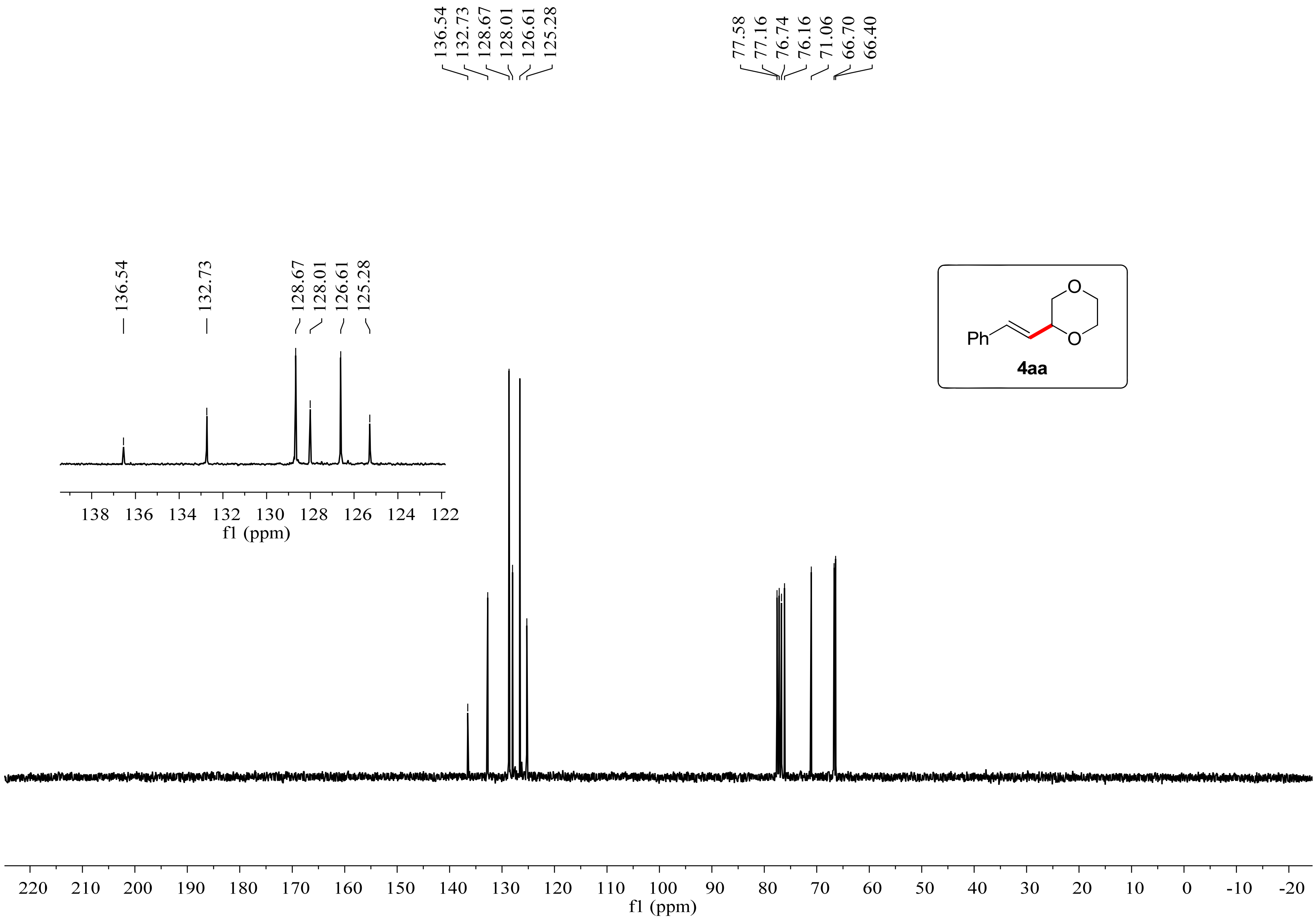
2.5
2.0
1.5
1.0
0.5
0.0
-0.5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128.01
126.61
125.28
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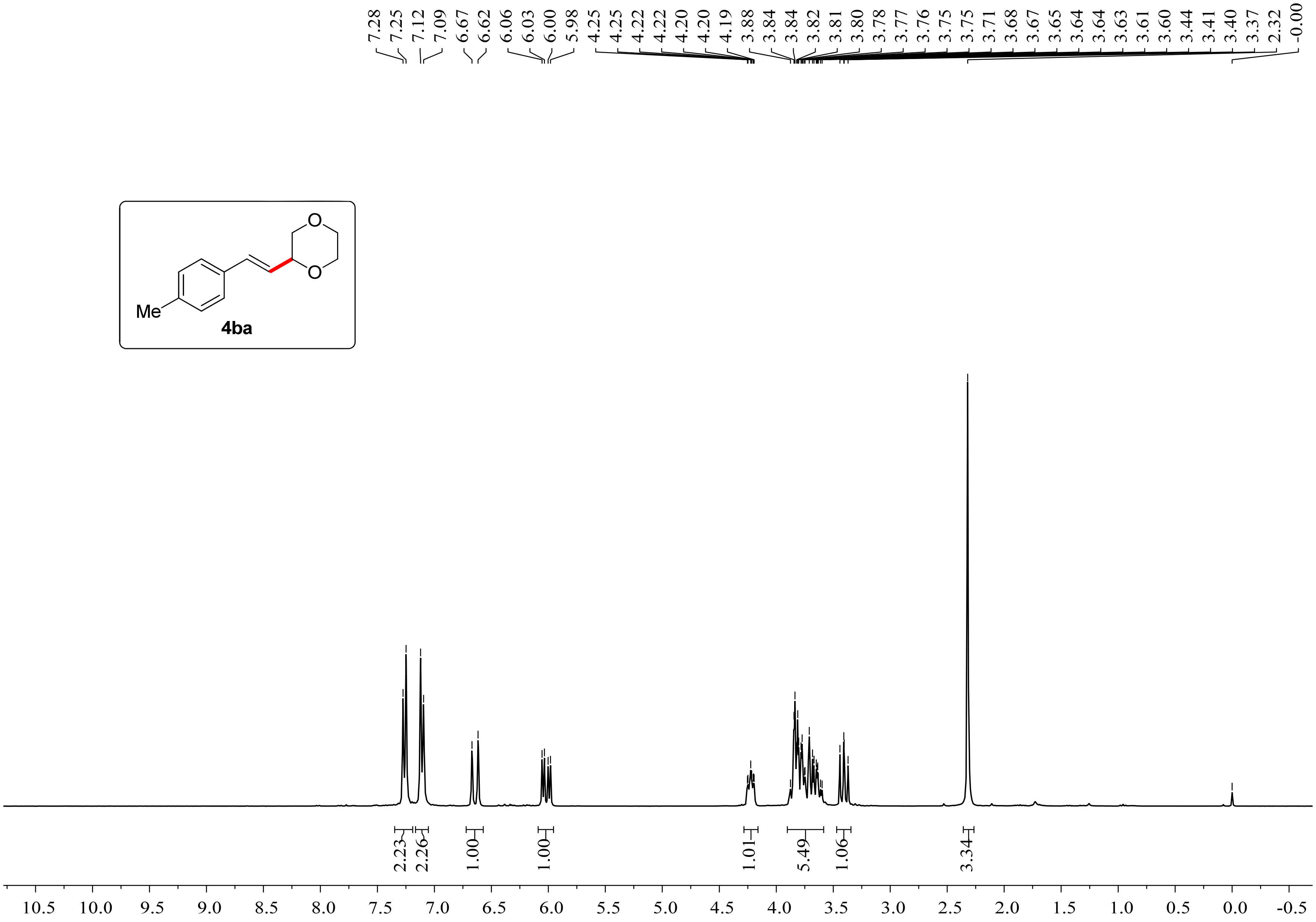
77.16
76.74
76.16
71.06
66.70
66.40
136.54
132.73
128.67
128.01
126.61
125.28
138 136 134 132 130 128 126 124 122
f1 (ppm)
Ph
O
O
4aa
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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7.12
7.09
6.67
6.62
6.06
6.03
6.00
5.98
4.25
4.25
4.22
4.22
4.20
4.20
4.19
3.88
3.84
3.84
3.82
3.81
3.80
3.78
3.77
3.76
3.75
3.75
3.71
3.68
3.67
3.65
3.64
3.64
3.63
3.61
3.60
3.44
3.41
3.40
3.37
2.32
-0.00
O
O
Me
4ba
2.23
2.26
1.00
1.00
1.01
5.49
1.06
3.34
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
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6.0
5.5
5.0
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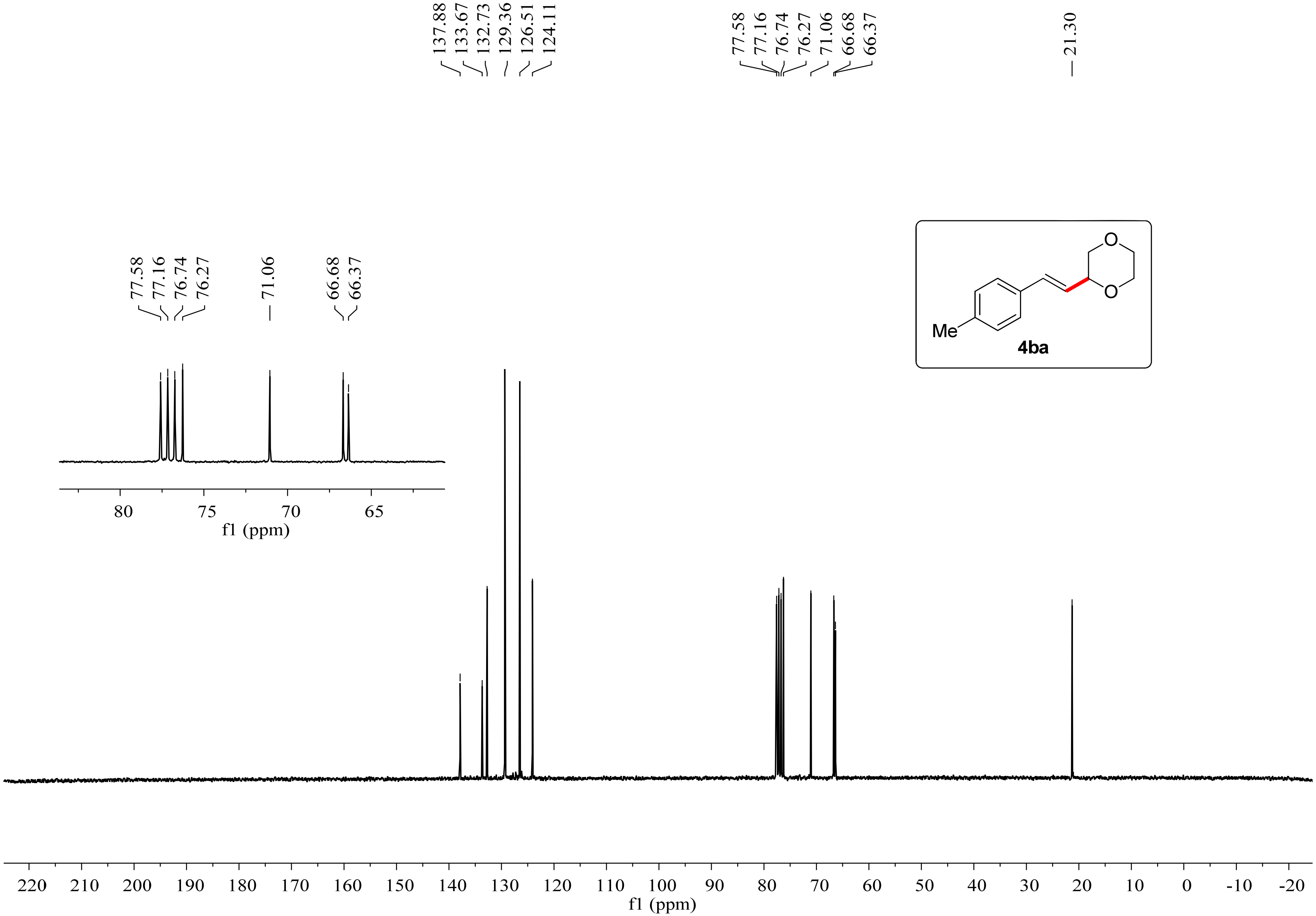
2.0
1.5
1.0
0.5
0.0
-0.5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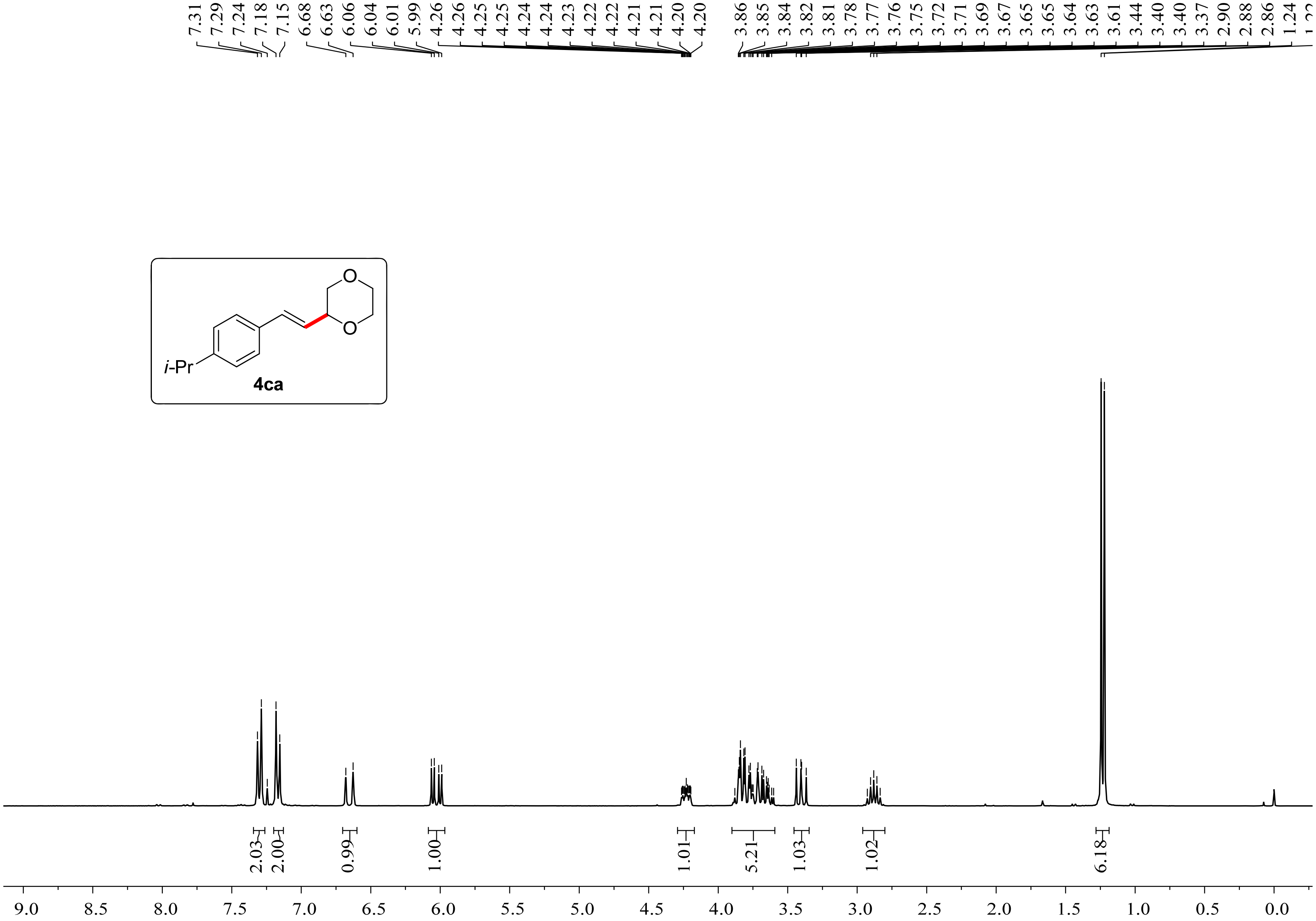
77.16
76.74
76.27
71.06
66.68
66.37
21.30
77.58
77.16
76.74
76.27
71.06
66.68
66.37
80
75
70
65
f1 (ppm)
Me
O
O
4ba
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)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6.63
6.06
6.04
6.01
5.99
4.26
4.26
4.25
4.25
4.24
4.24
4.23
4.22
4.22
4.21
4.21
4.20
4.20
3.86
3.85
3.84
3.82
3.81
3.78
3.77
3.76
3.75
3.72
3.71
3.69
3.67
3.65
3.65
3.64
3.63
3.61
3.44
3.40
3.40
3.37
2.90
2.88
2.86
1.24
O
O
i-Pr
4ca
2.03
2.00
0.99
1.00
1.01
5.21
1.03
1.02
6.18
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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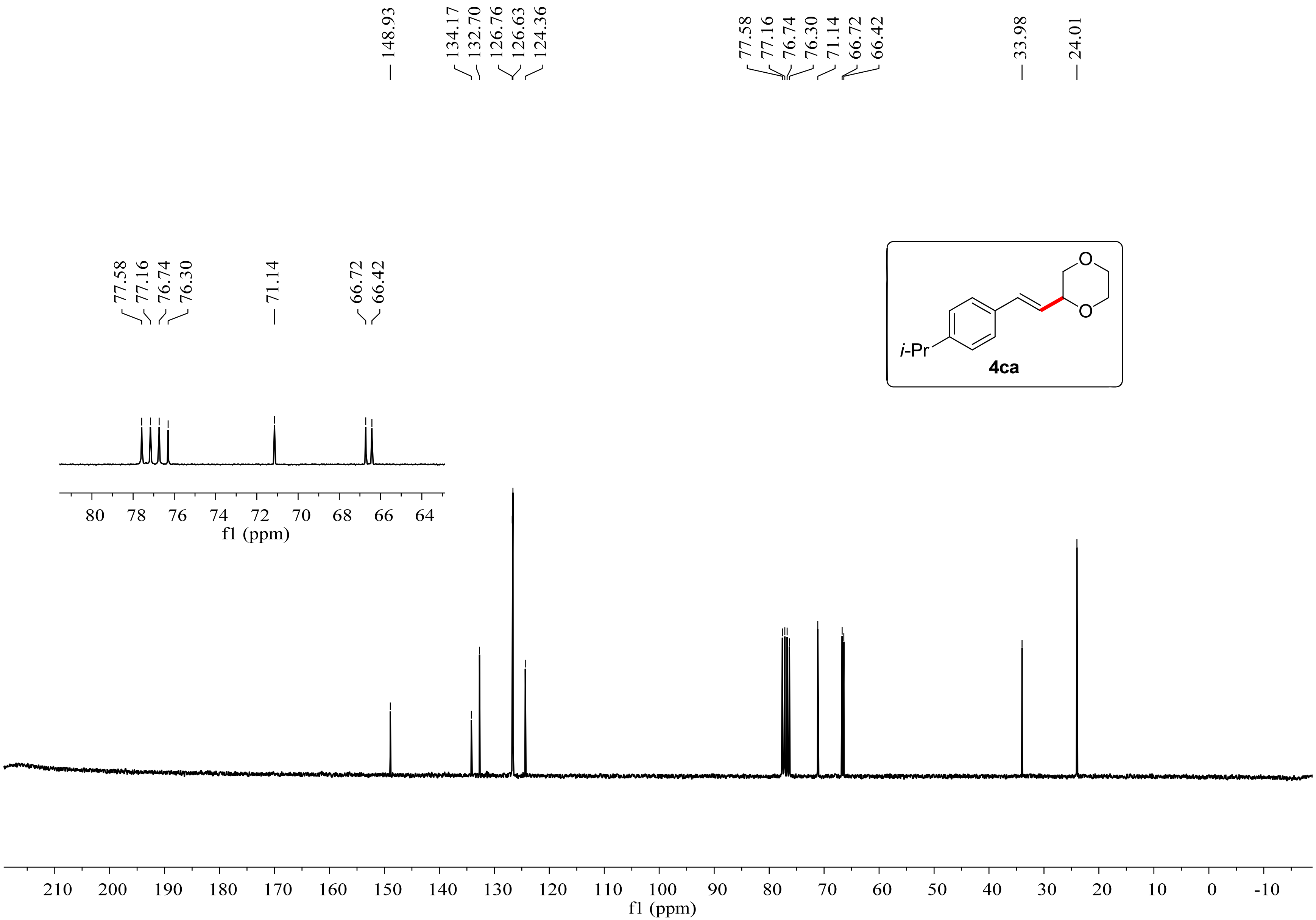
0.0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71.14
66.72
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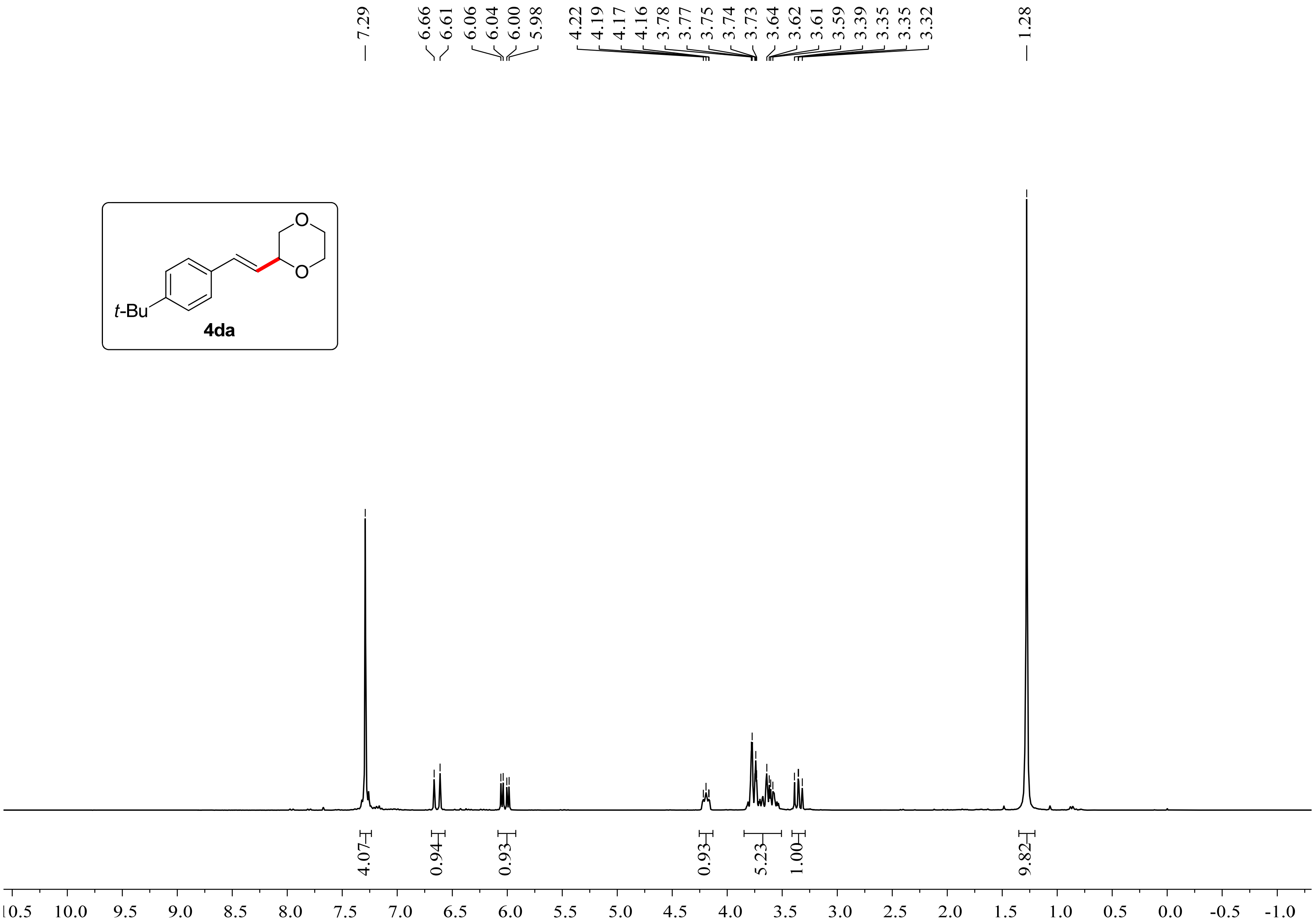
33.98
24.01
77.58
77.16
76.74
76.30
71.14
66.72
66.42
80 78 76 74 72 70 68 66 64
f1 (ppm)
O
O
i-Pr
4ca
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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6.66
6.61
6.06
6.04
6.00
5.98
4.22
4.19
4.17
4.16
3.78
3.77
3.75
3.74
3.73
3.64
3.62
3.61
3.59
3.39
3.35
3.35
3.32
1.28
O
O
t-Bu
4da
4.07
0.94
0.93
0.93
5.23
1.00
9.82
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
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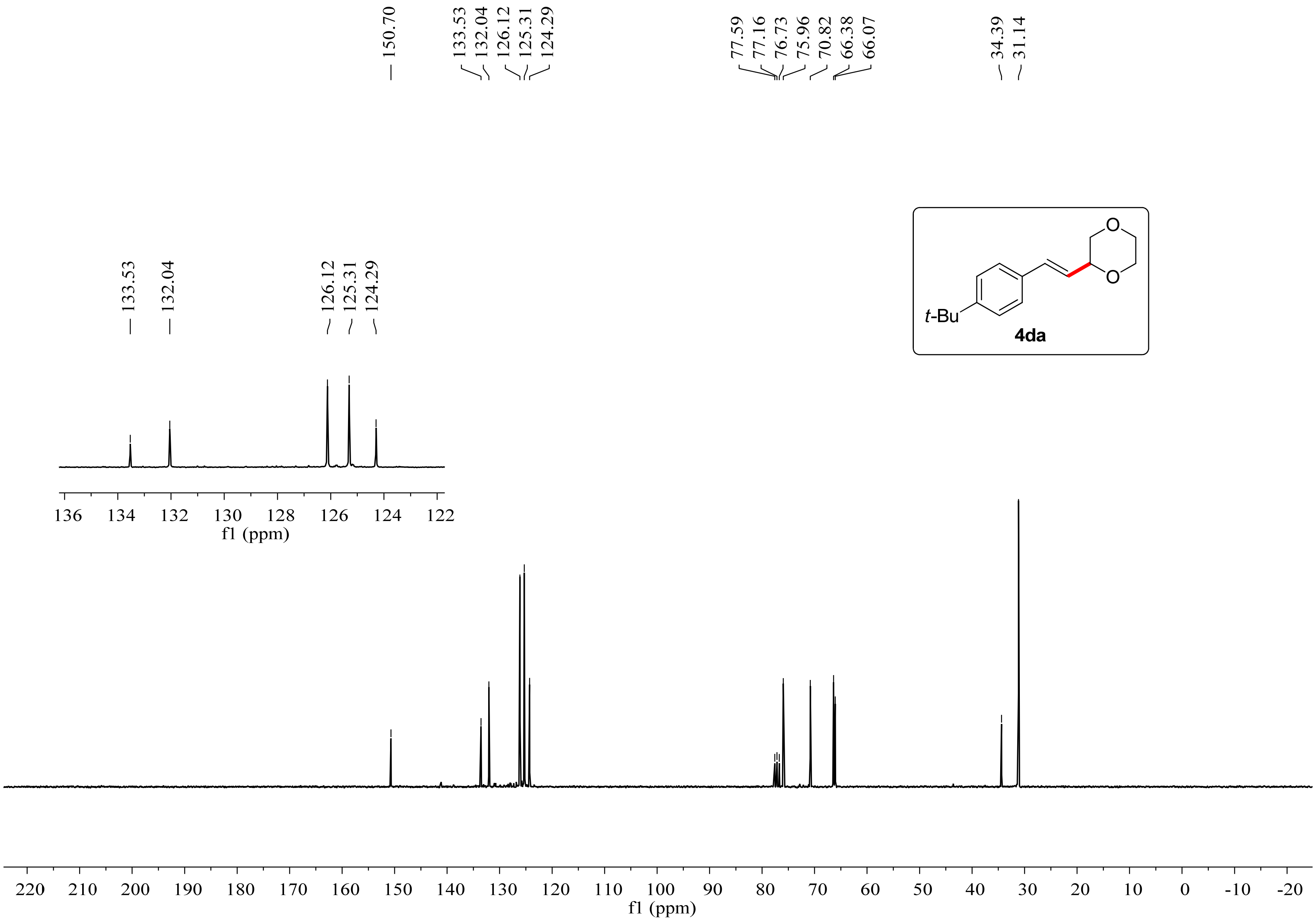
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0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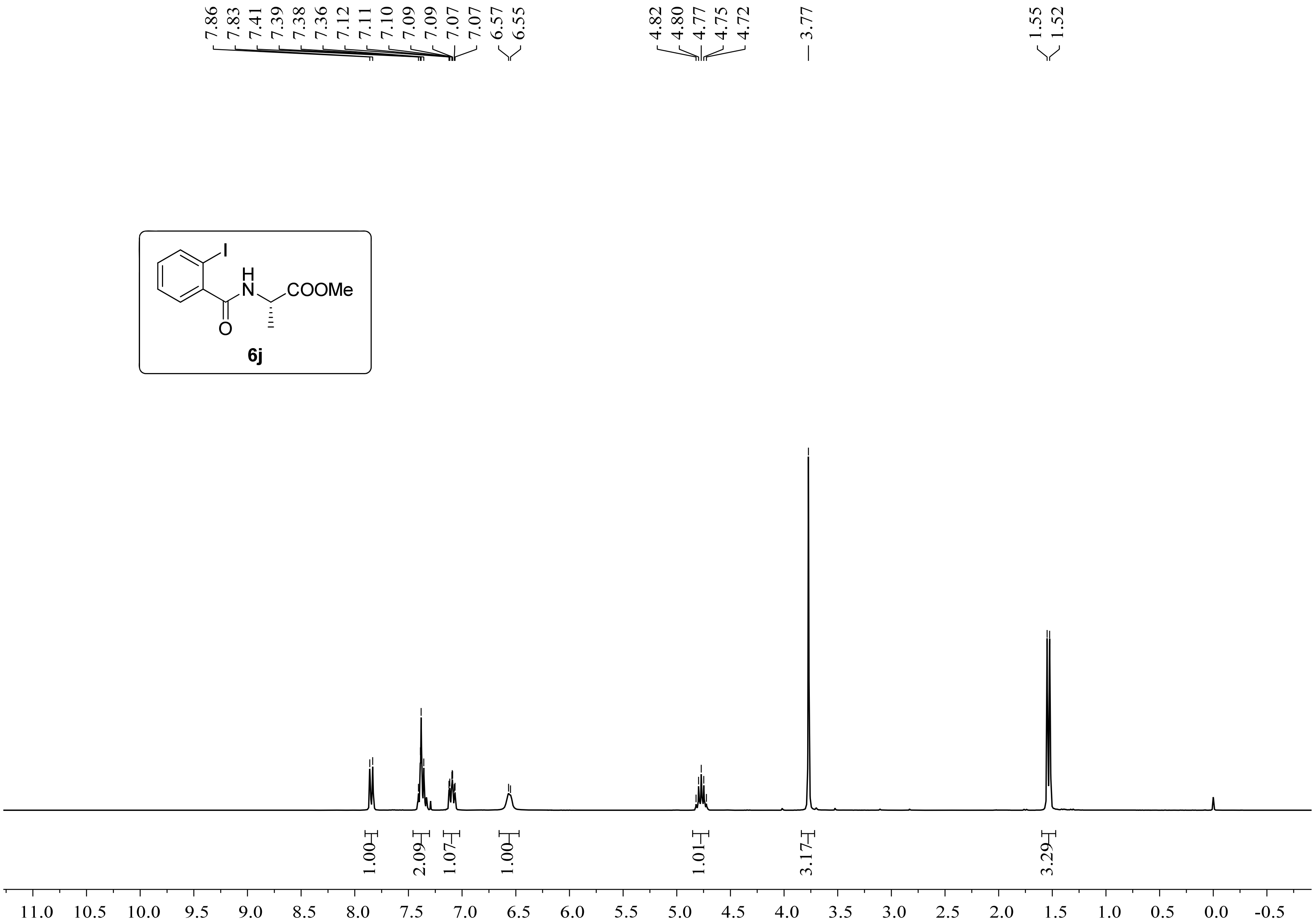
124.29
77.59
77.16
76.73
75.96
70.82
66.38
66.07
34.39
31.14
133.53
132.04
126.12
125.31
124.29
136 134 132 130 128 126 124 122
f1 (ppm)
O
O
t-Bu
4da
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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7.38
7.36
7.12
7.11
7.10
7.09
7.09
7.07
7.07
6.57
6.55
4.82
4.80
4.77
4.75
4.72
3.77
1.55
1.52
I
H
N
COOMe
O
6j
1.00
2.09
1.07
1.00
1.01
3.17
3.29
11.0
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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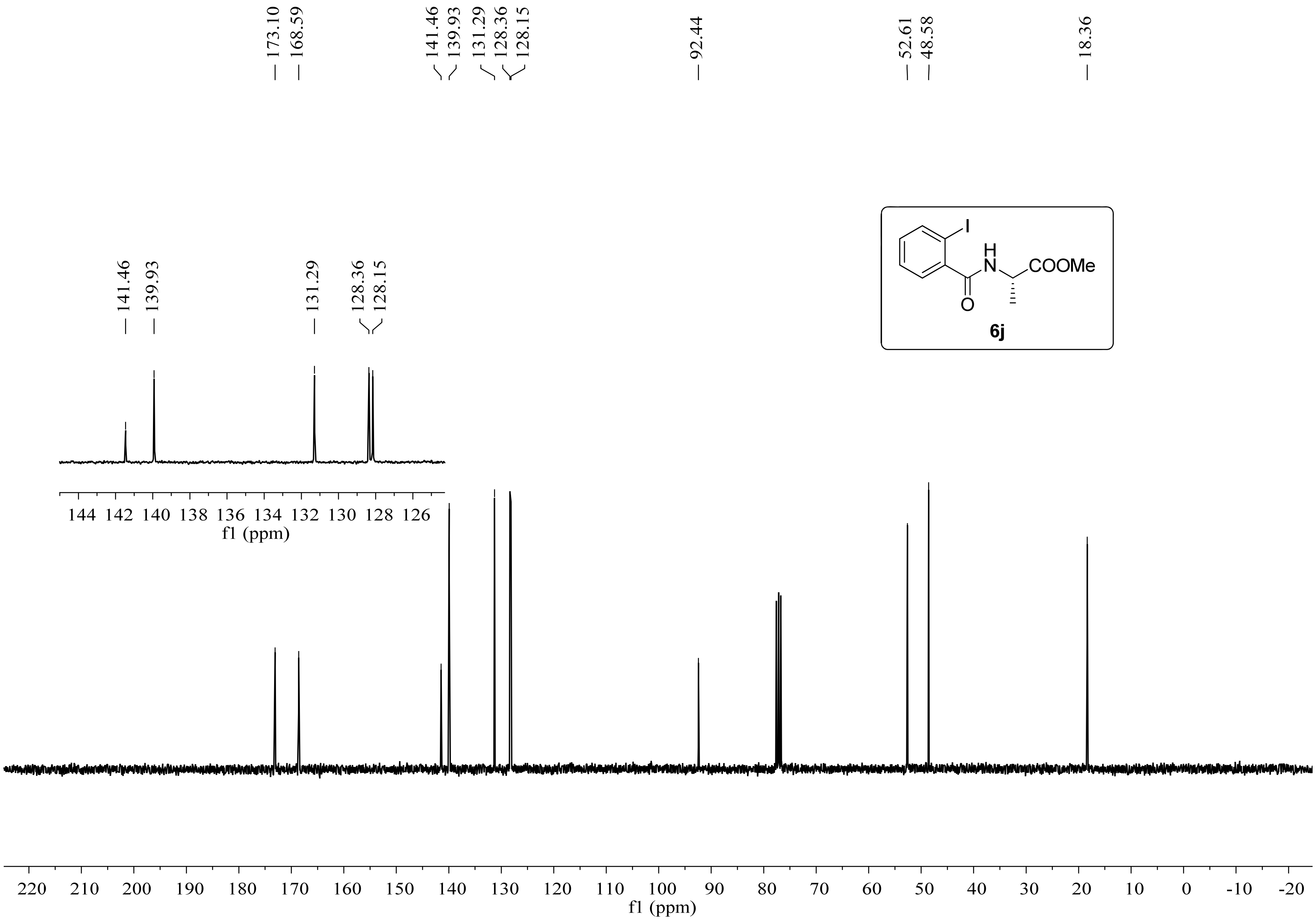
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5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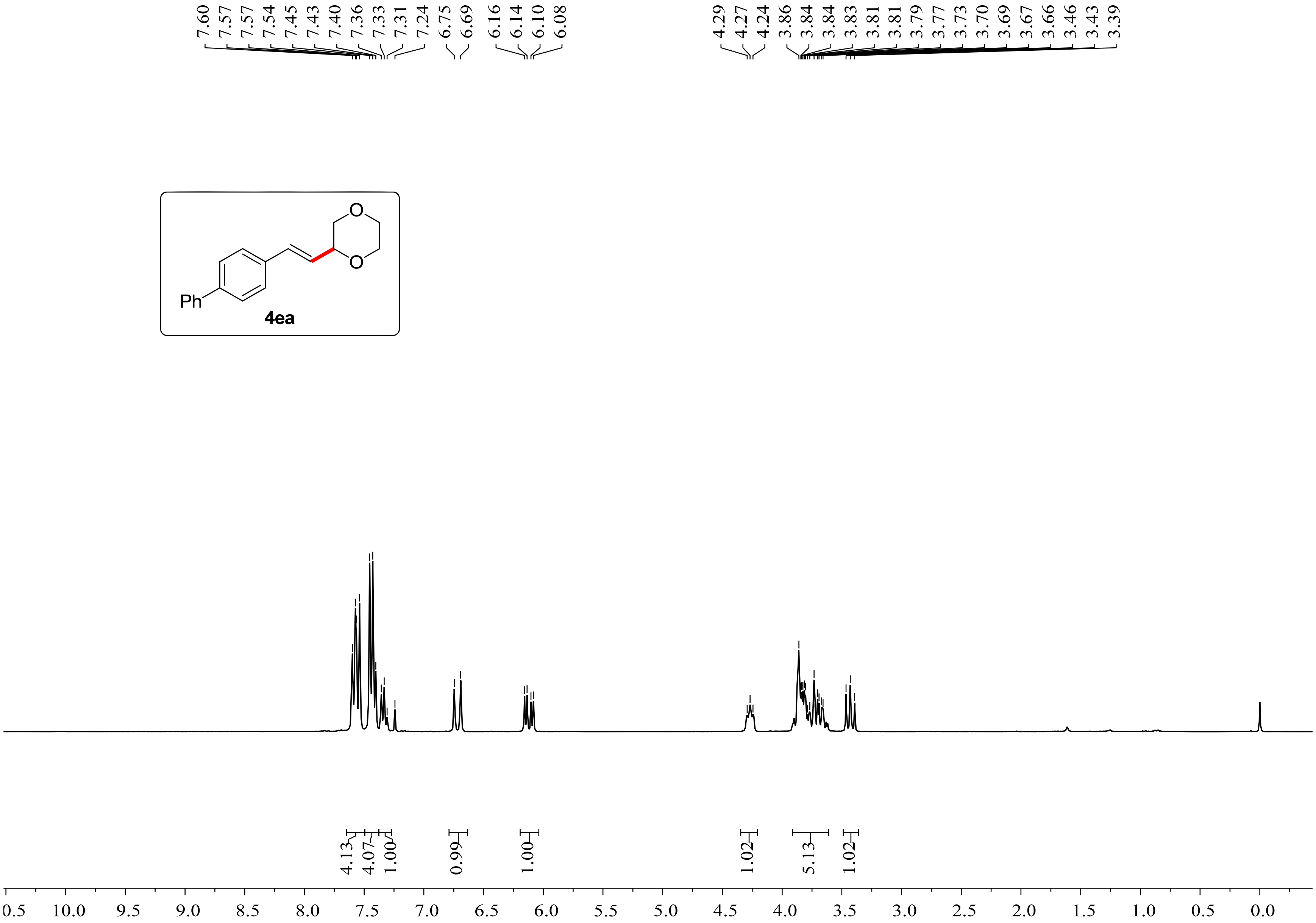
139.93
131.29
128.36
128.15
92.44
52.61
48.58
18.36
141.46
139.93
131.29
128.36
128.15
144 142 140 138 136 134 132 130 128 126
f1 (ppm)
I
H
N
COOMe
O
6j
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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7.57
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7.43
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7.36
7.33
7.31
7.24
6.75
6.69
6.16
6.14
6.10
6.08
4.29
4.27
4.24
3.86
3.84
3.84
3.83
3.81
3.81
3.79
3.77
3.73
3.70
3.69
3.67
3.66
3.46
3.43
3.39
O
O
Ph
4ea
4.13
4.07
1.00
0.99
1.00
1.02
5.13
1.02
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.0
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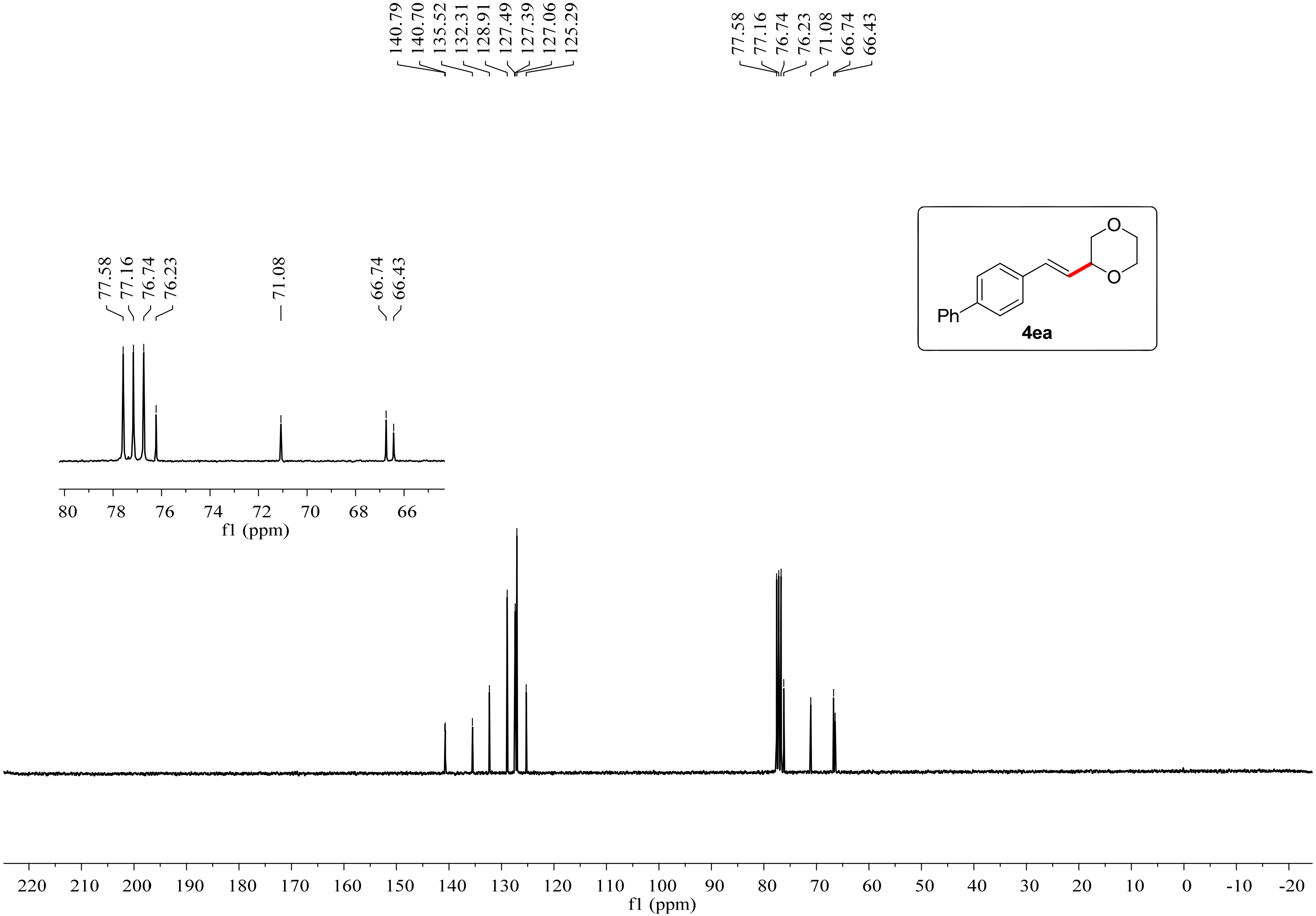
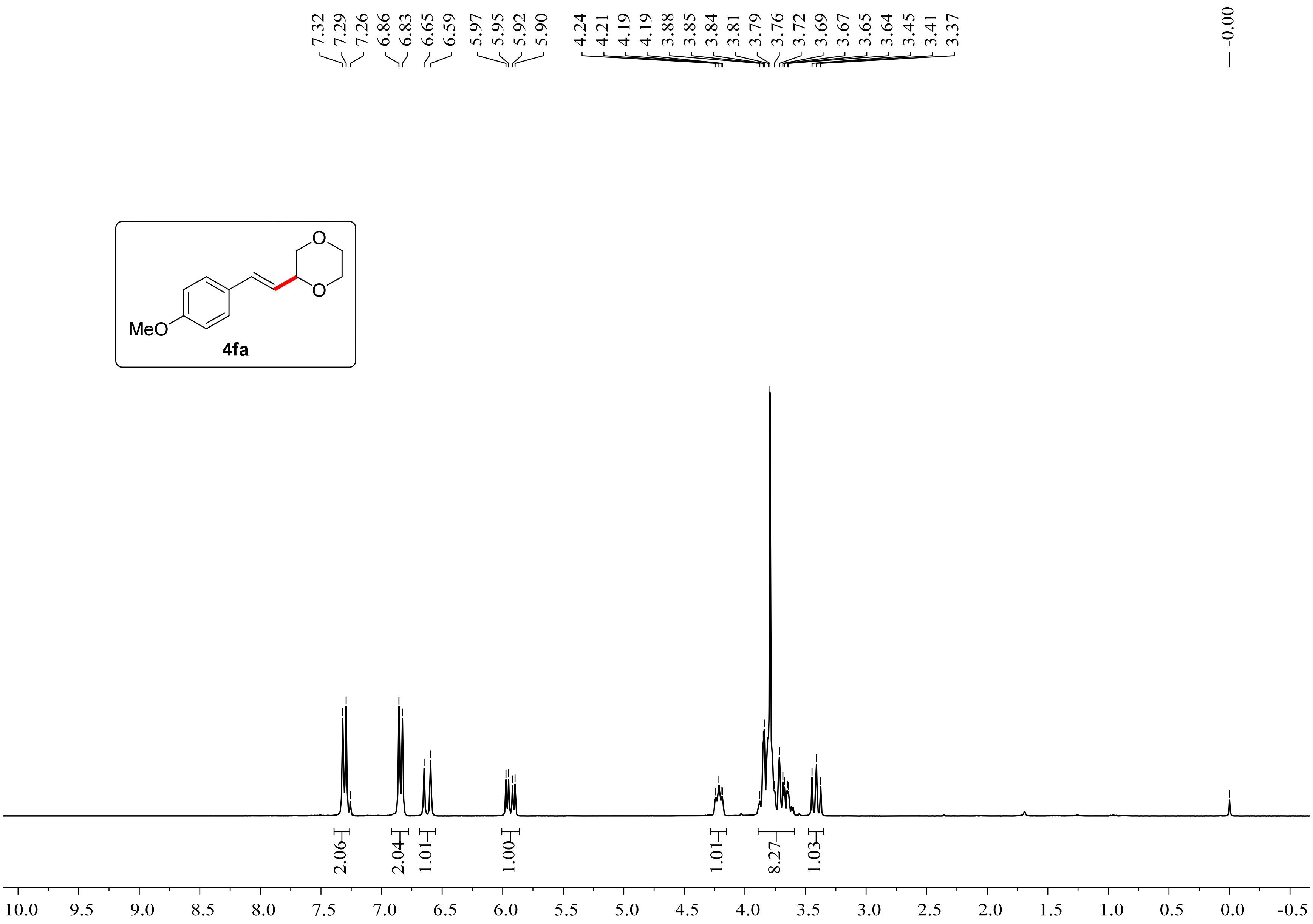
3.0
2.5
2.0
1.5
1.0
0.5
0.0


140.79
140.70
135.52
132.31
128.91
127.49
127.39
127.06
125.29
77.58
77.16
76.74
76.23
71.08
66.74
66.43
77.58
77.16
76.74
76.23
71.08
66.74
66.43
80
78
76
74
72
70
68
66
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)

O
O
Ph

**4ea**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5.90
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4.21
4.19
4.19
3.88
3.85
3.84
3.81
3.79
3.76
3.72
3.69
3.67
3.65
3.64
3.45
3.41
3.37
-0.00
O
O
MeO
4fa
2.06
2.04
1.01
1.00
1.01
8.27
1.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
2.5
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1.0
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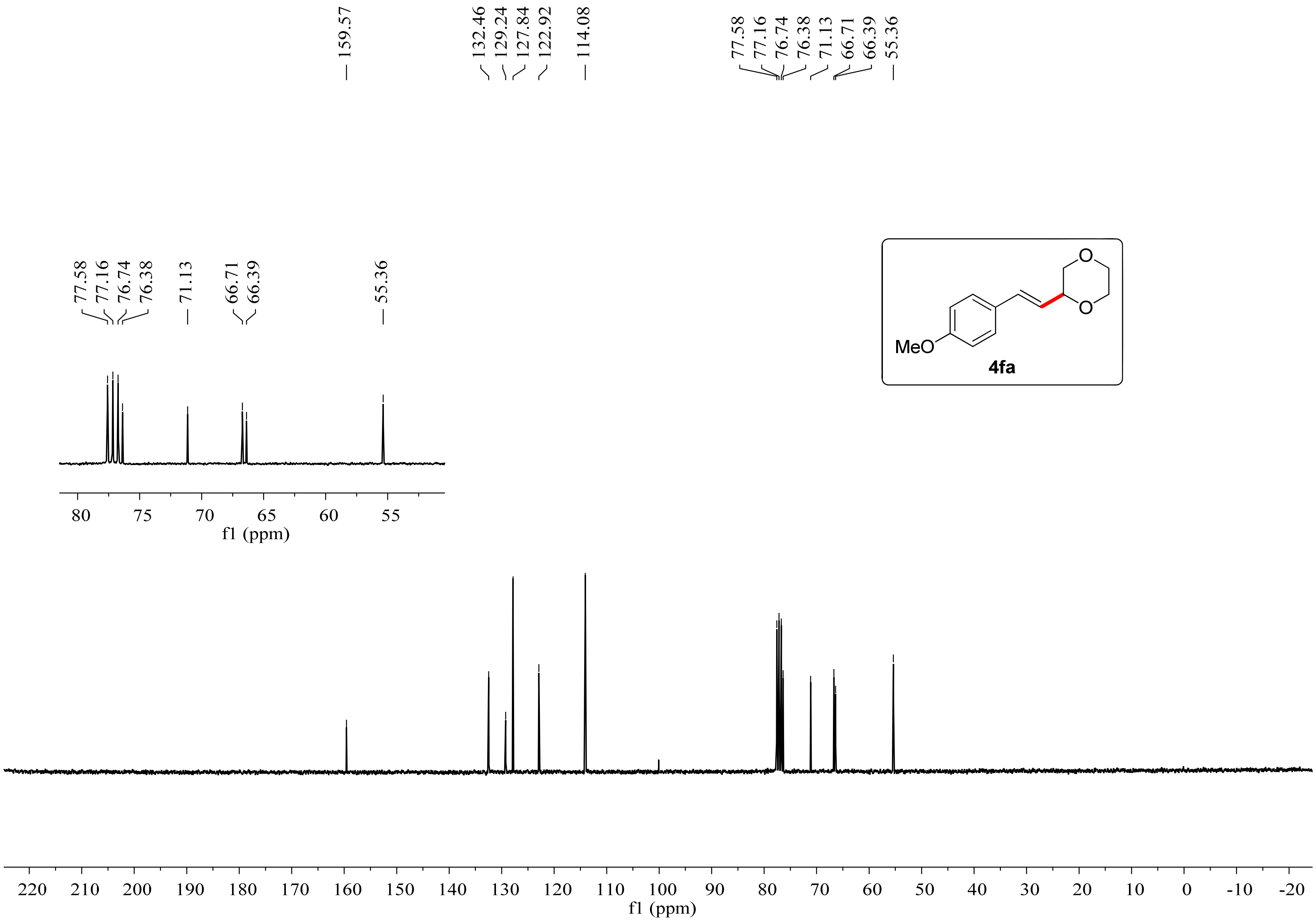
0.0
-0.5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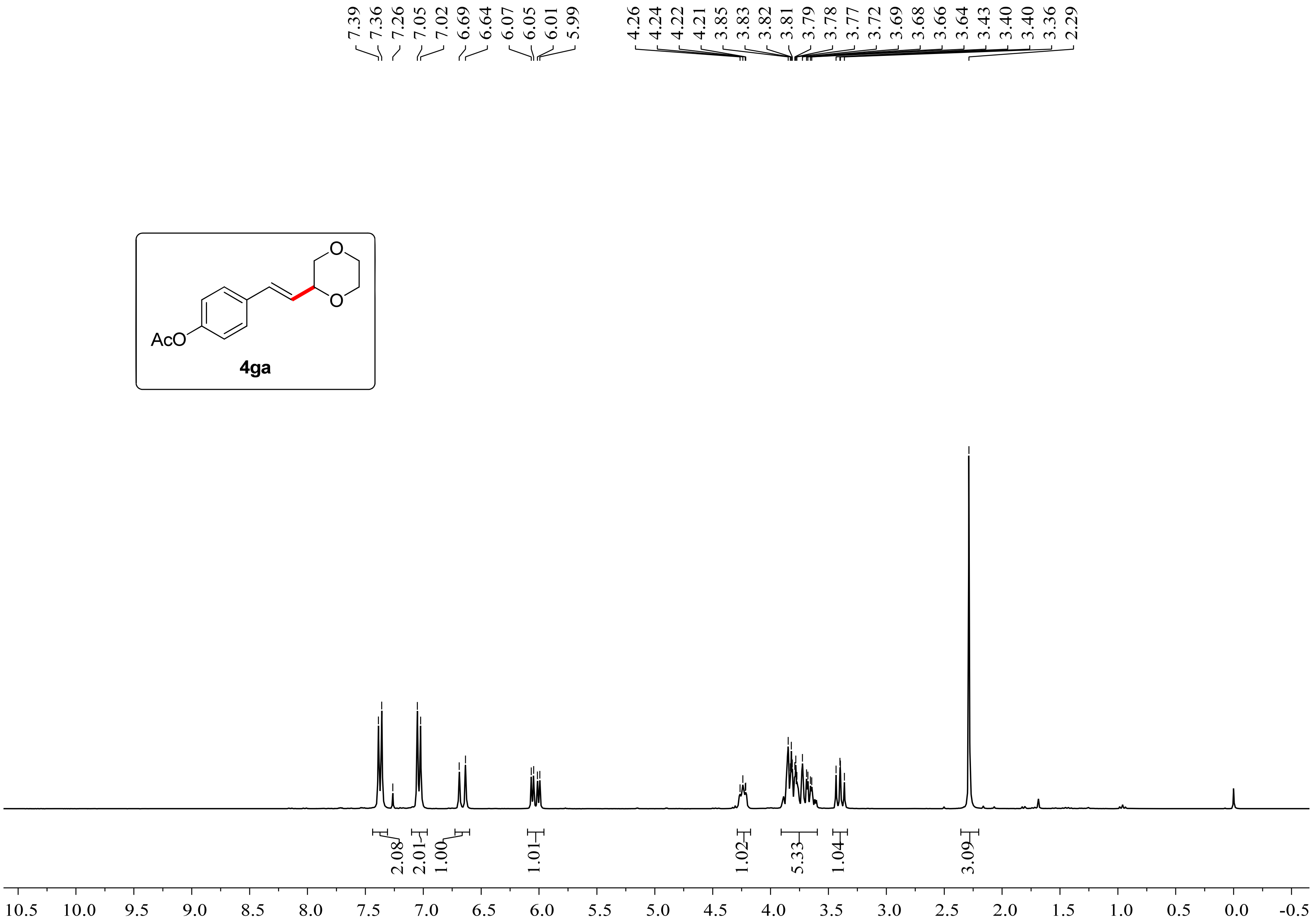
122.92
114.08
77.58
77.16
76.74
76.38
71.13
66.71
66.39
55.36
77.58
77.16
76.74
76.38
71.13
66.71
66.39
55.36
80
75
70
65
60
55
f1 (ppm)
MeO
O
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

**4fa**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6.01
5.99
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4.24
4.22
4.21
3.85
3.83
3.82
3.81
3.79
3.78
3.77
3.72
3.69
3.68
3.66
3.64
3.43
3.40
3.40
3.36
2.29
AcO
O
O
4ga
2.08
2.01
1.00
1.01
1.02
5.33
1.04
3.09
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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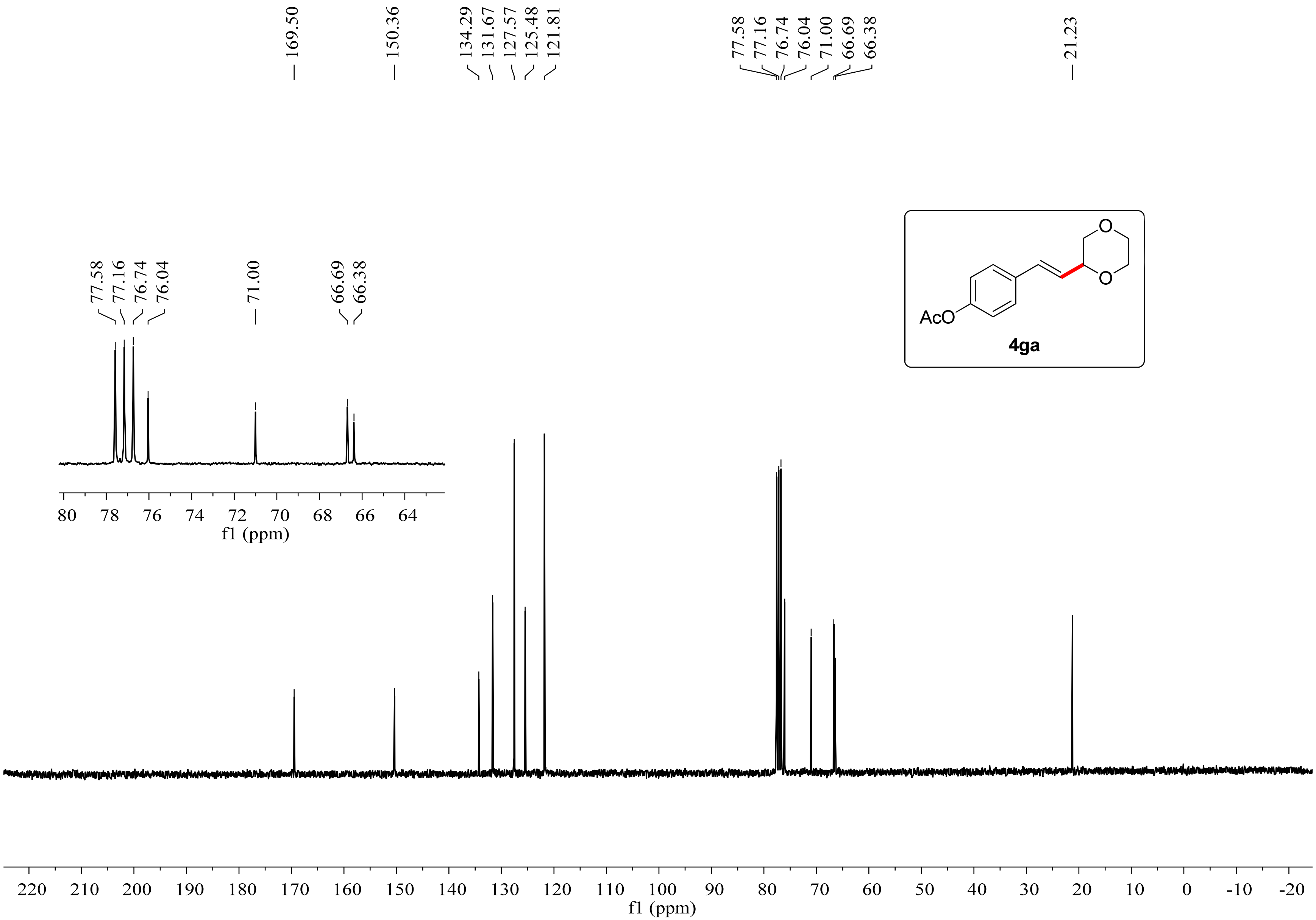
0.0
-0.5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125.48
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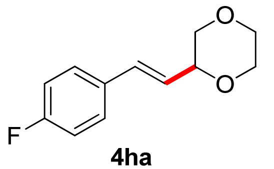
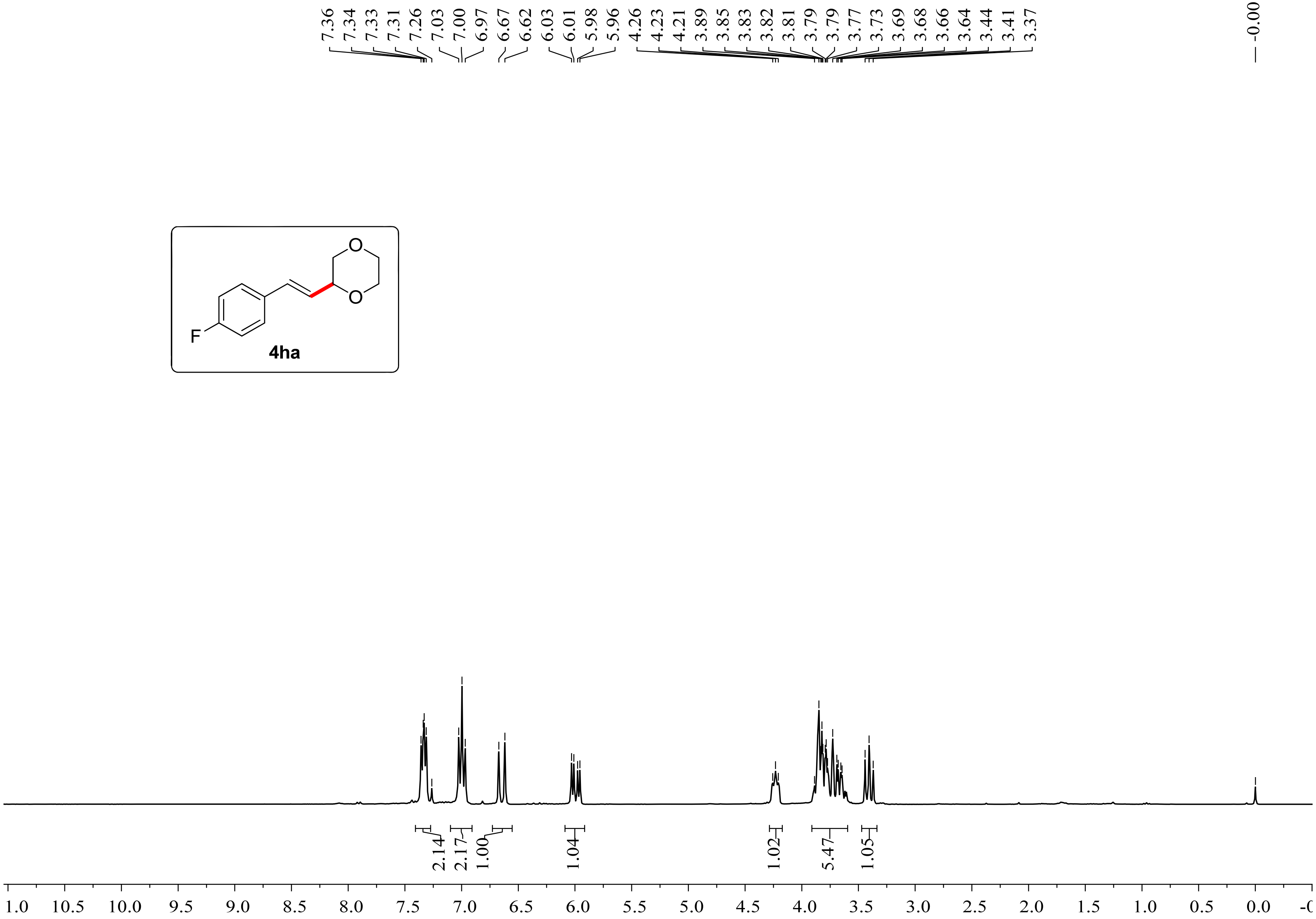
77.16
76.74
76.04
71.00
66.69
66.38
21.23
AcO
O
O
77.58
77.16
76.74
76.04
71.00
66.69
66.38
80 78 76 74 72 70 68 66 64
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

**4ga**


O
O
F

**4ha**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6.97
6.67
6.62
6.03
6.01
5.98
5.96
4.26
4.23
4.21
3.89
3.85
3.83
3.82
3.81
3.79
3.79
3.77
3.73
3.69
3.68
3.66
3.64
3.44
3.41
3.37
-0.00
2.14
2.17
1.00
1.04
1.02
5.47
1.05
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.0
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3.0
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2.0
1.5
1.0
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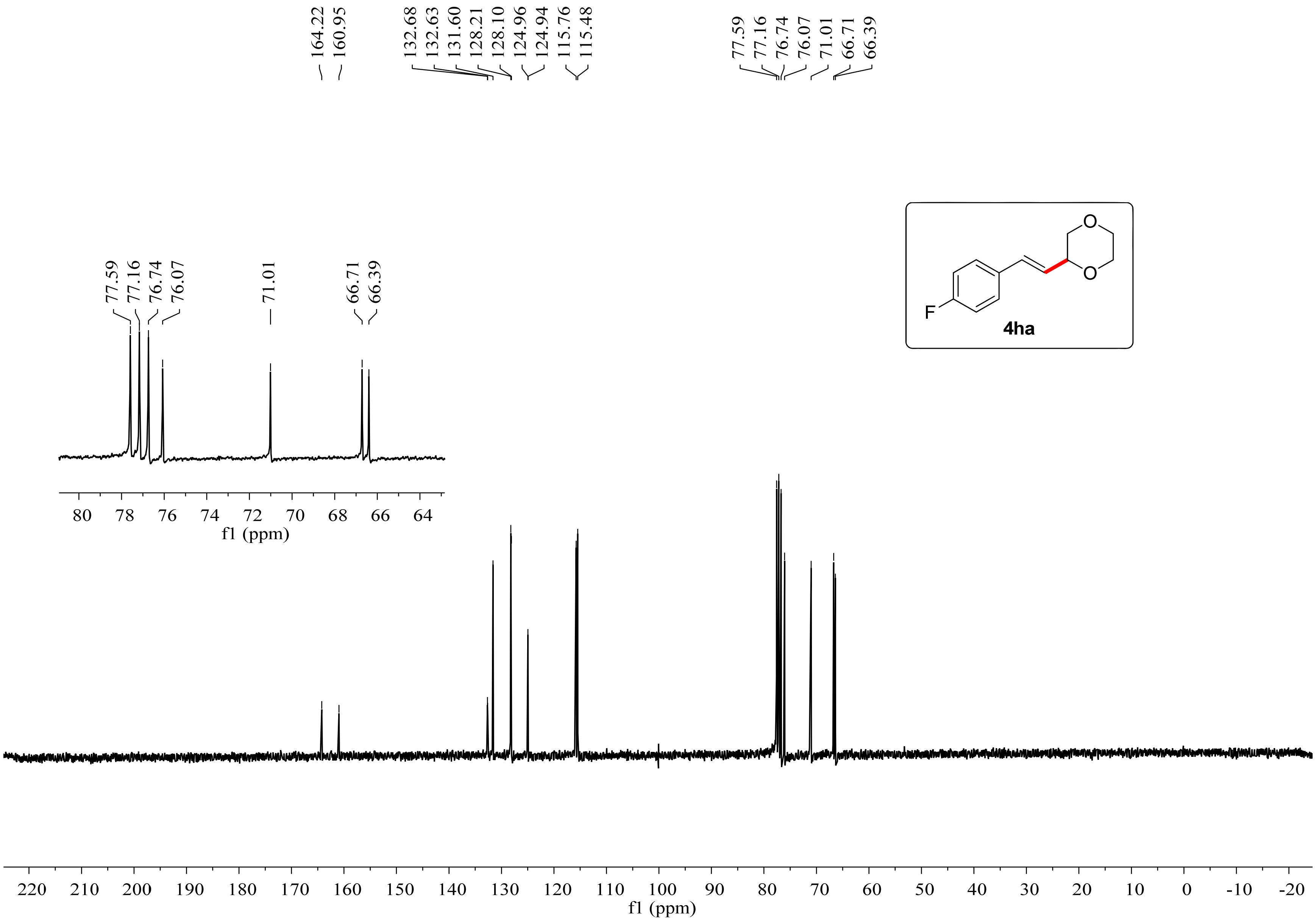
0.0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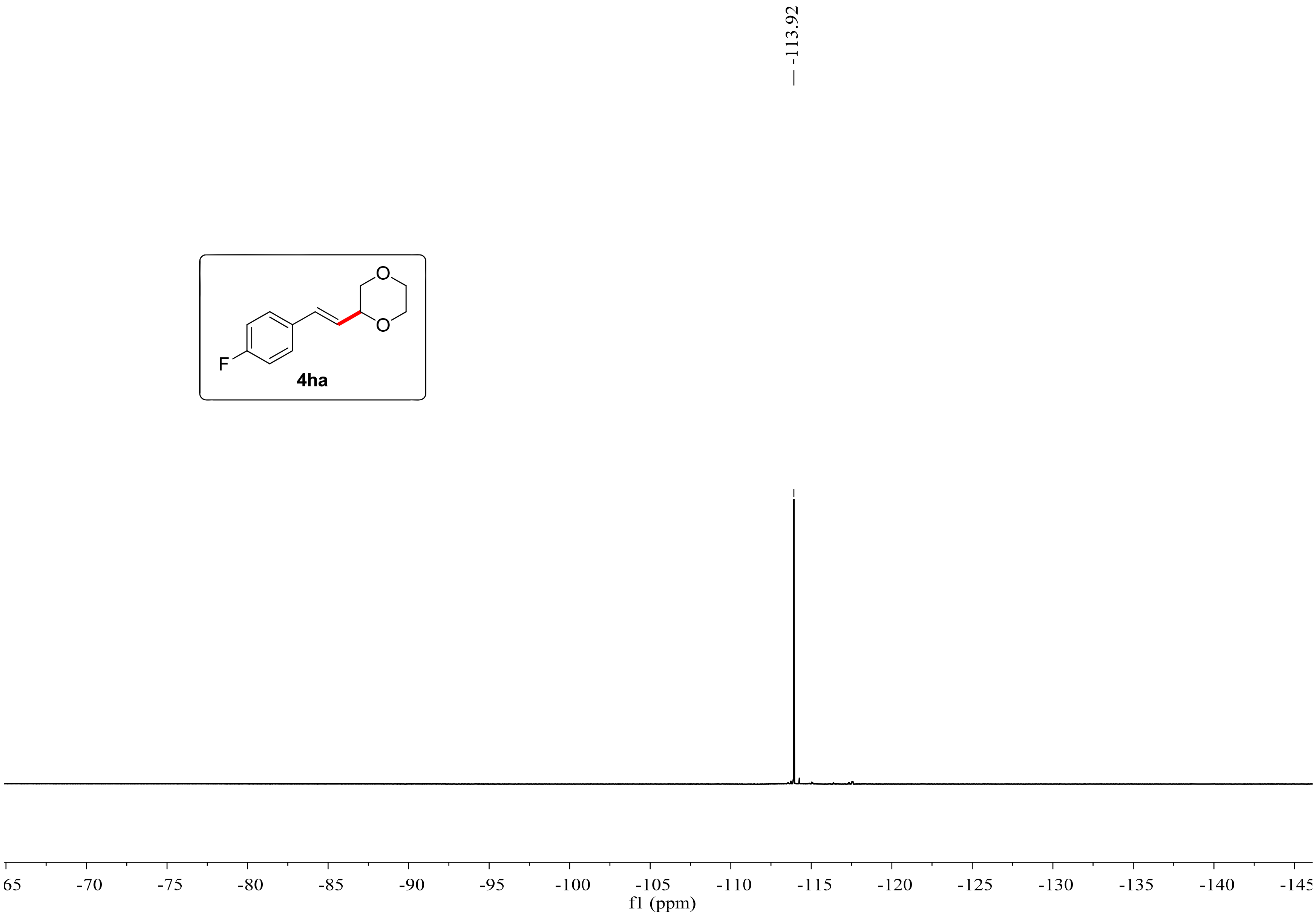
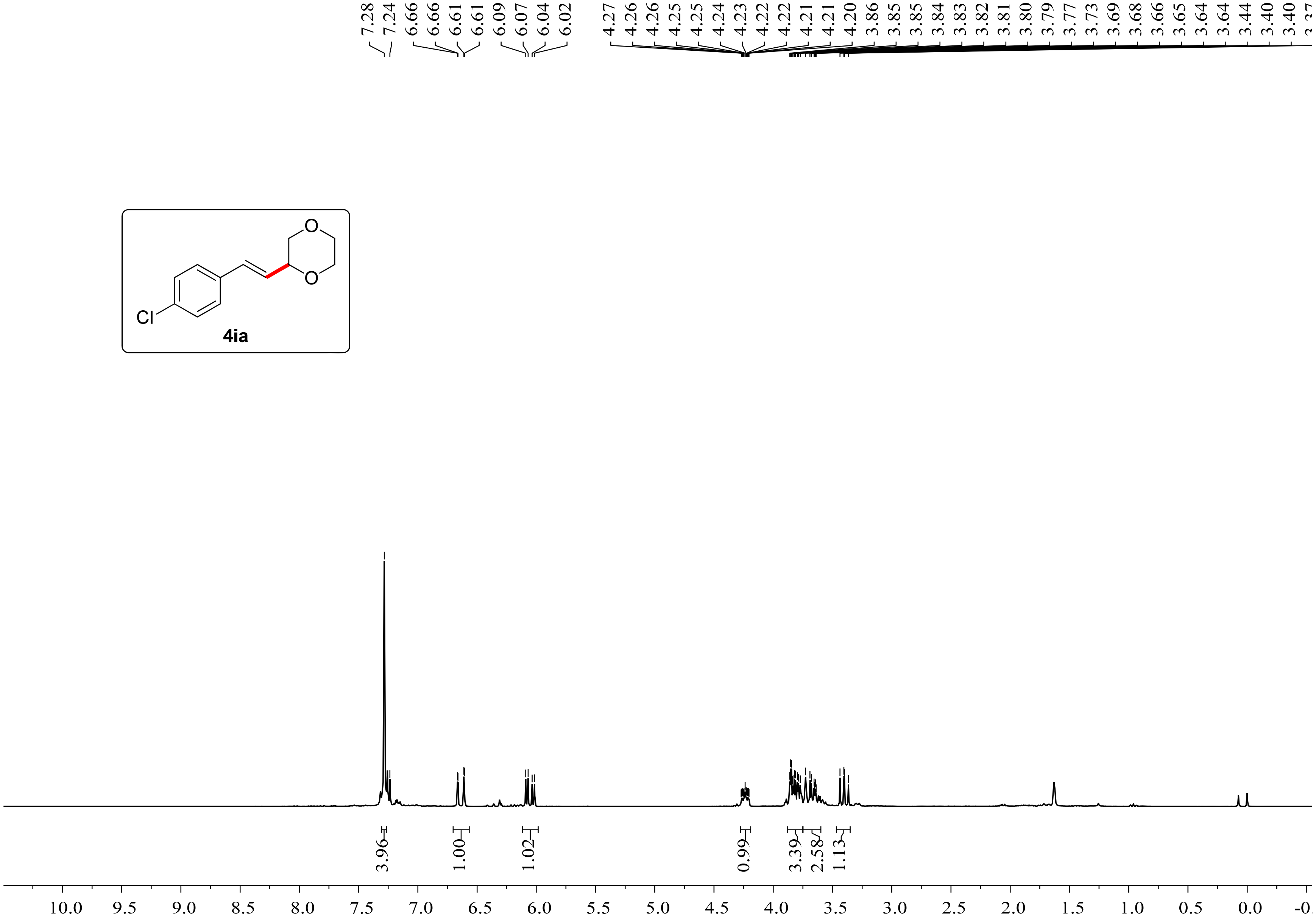
160.95
132.68
132.63
131.60
128.21
128.10
124.96
124.94
115.76
115.48
77.59
77.16
76.74
76.07
71.01
66.71
66.39
4ha
F
O
O
80
78
76
74
72
70
68
66
64
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


-113.92
F
O
O
4ha
65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
f1 (ppm)

O
O
Cl

**4ia**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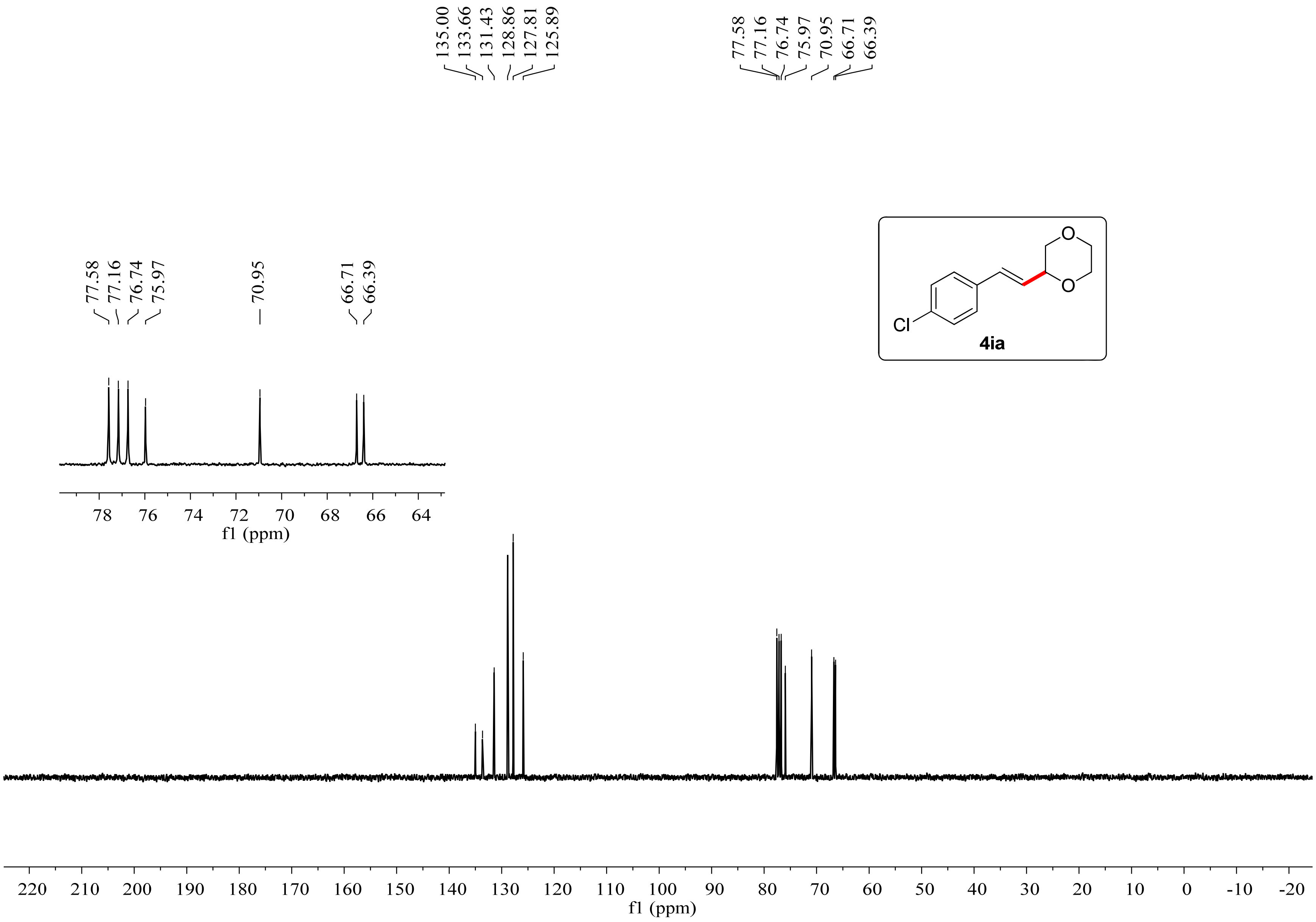
6.61
6.09
6.07
6.04
6.02
4.27
4.26
4.26
4.25
4.25
4.24
4.23
4.22
4.22
4.21
4.21
4.20
3.86
3.85
3.85
3.84
3.83
3.82
3.81
3.80
3.79
3.77
3.73
3.69
3.68
3.66
3.65
3.64
3.64
3.44
3.40
3.40
3.96
1.00
1.02
0.99
3.39
2.58
1.13
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.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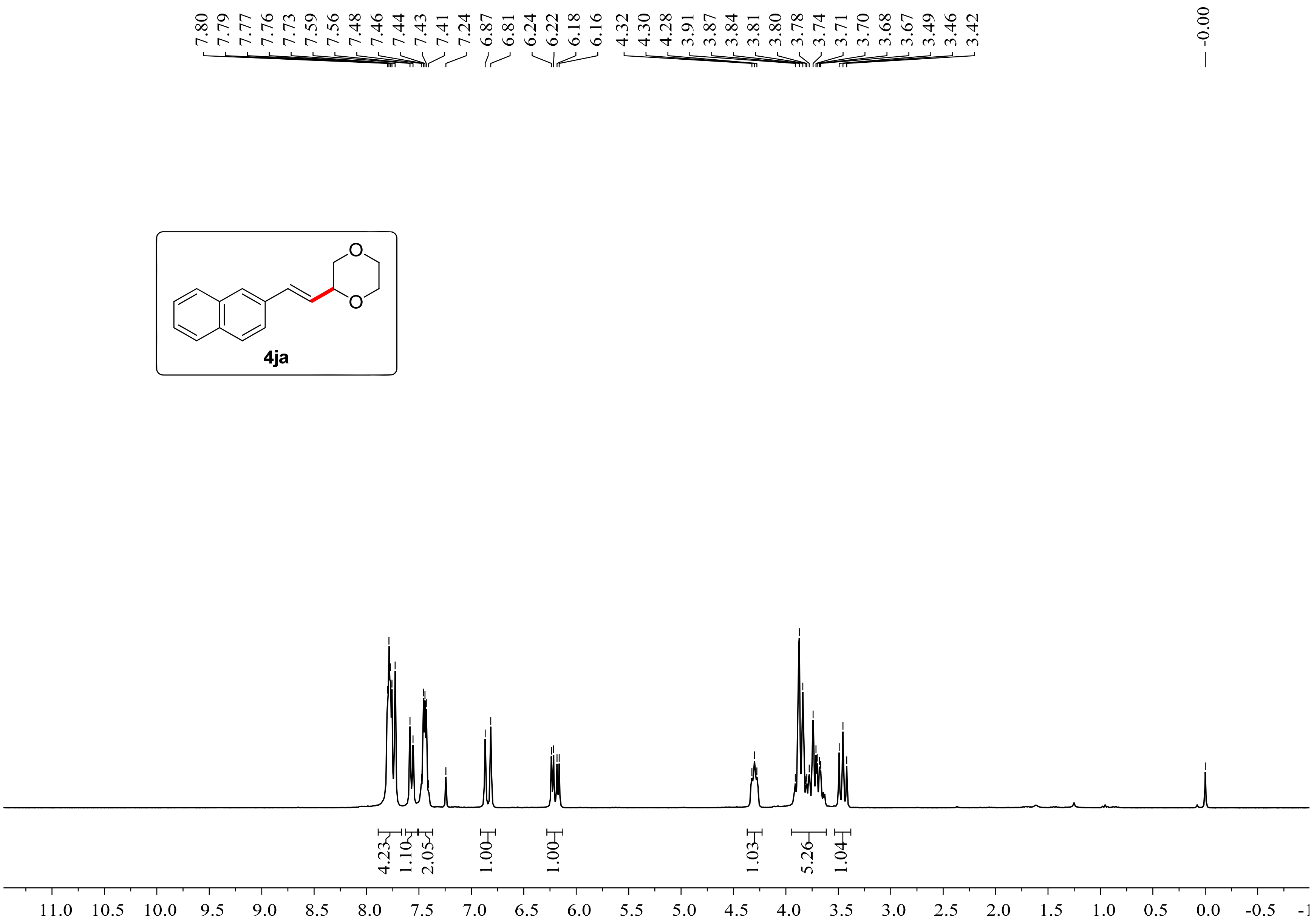
127.81
125.89
77.58
77.16
76.74
75.97
70.95
66.71
66.39
77.58
77.16
76.74
75.97
70.95
66.71
66.39
78 76 74 72 70 68 66 64
f1 (ppm)
Cl
O
O
4ia
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)



4ja

7.80
7.79
7.77
7.76
7.73
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7.48
7.46
7.44
7.43
7.41
7.24
6.87
6.81
6.24
6.22
6.18
6.16
4.32
4.30
4.28
3.91
3.87
3.84
3.81
3.80
3.78
3.74
3.71
3.70
3.68
3.67
3.49
3.46
3.42
-0.00
O
O
4.23
1.10
2.05
1.00
1.00
1.03
5.26
1.04
11.0
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
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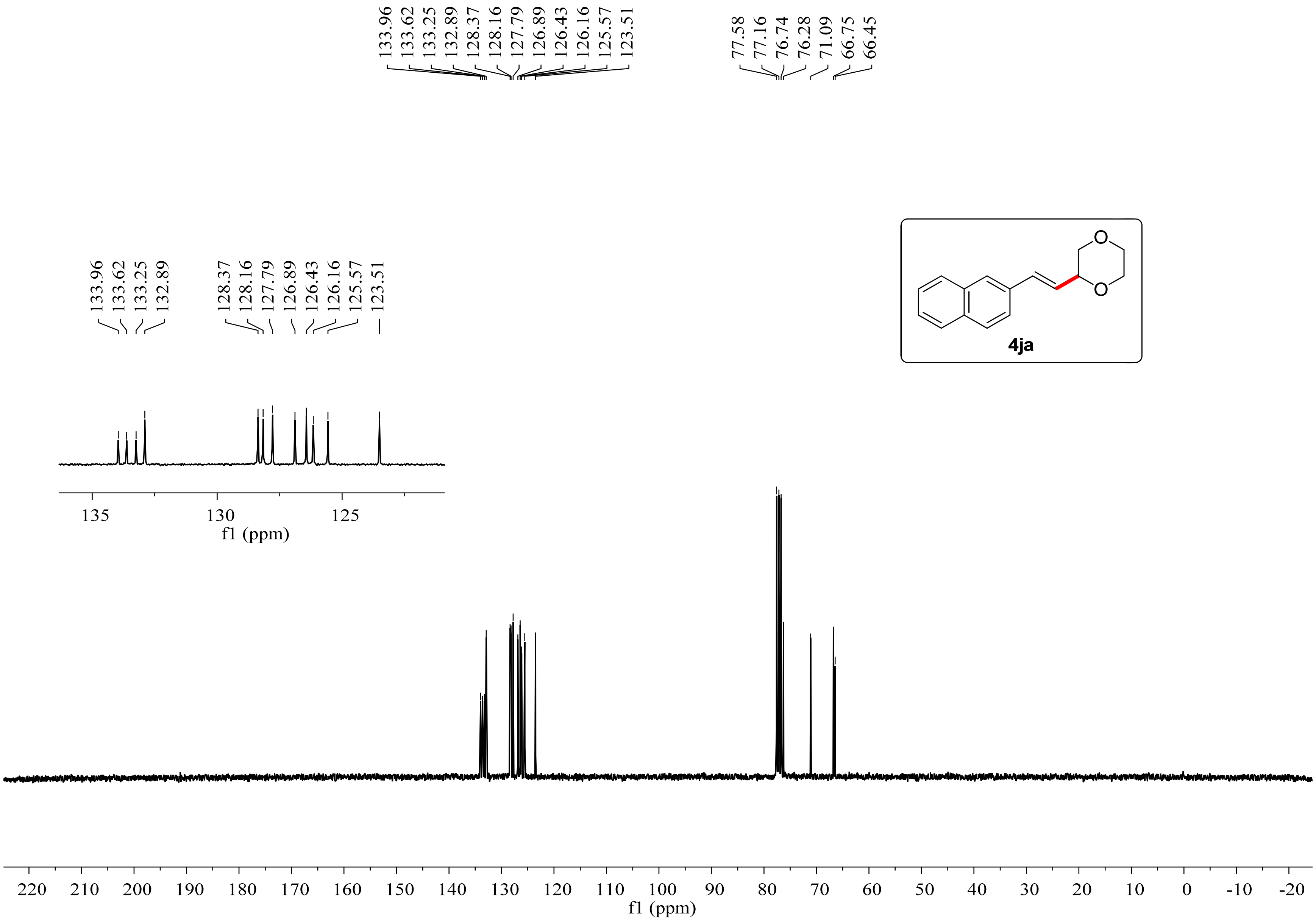
2.0
1.5
1.0
0.5
0.0
-0.5
-1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128.16
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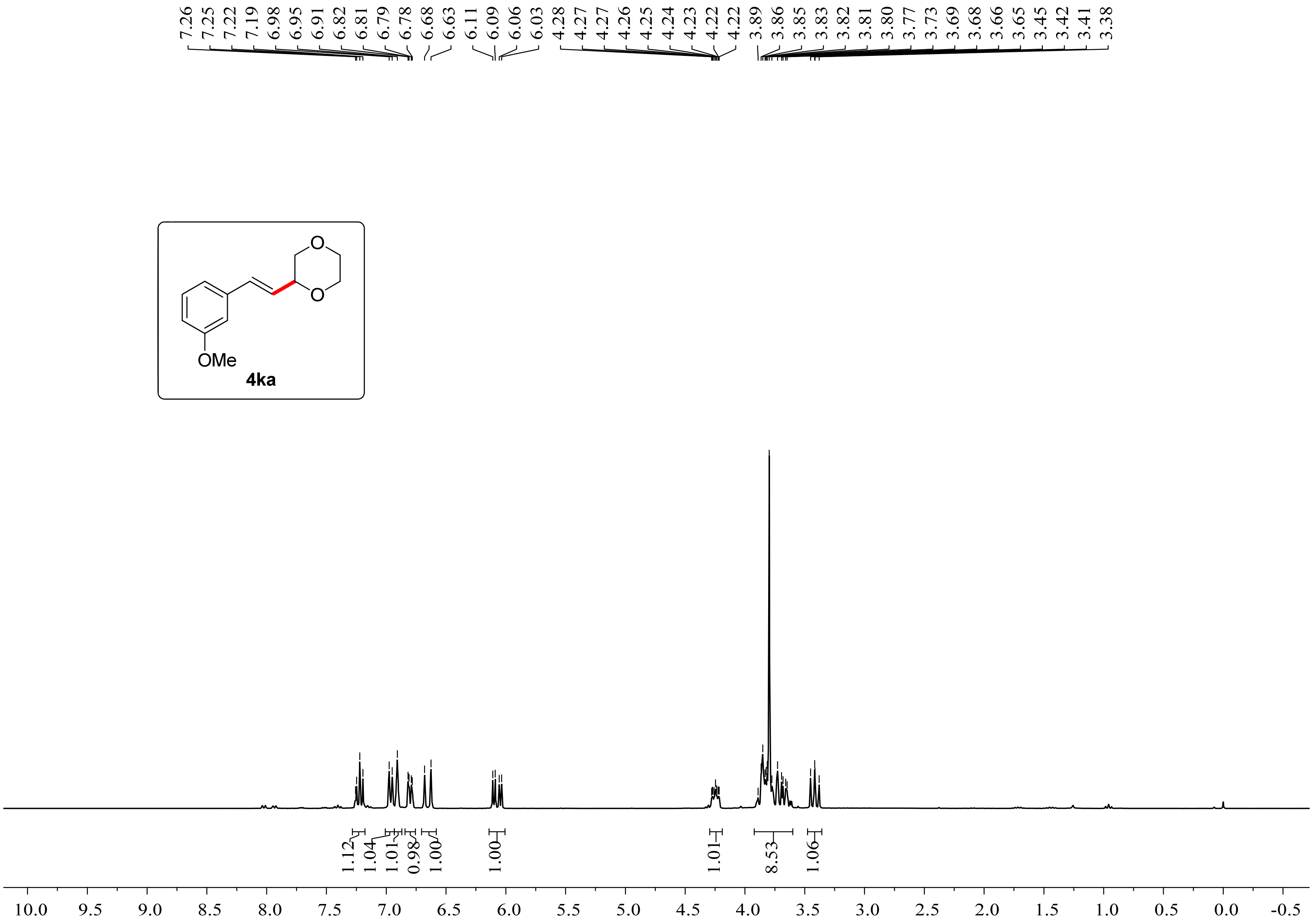
126.89
126.43
126.16
125.57
123.51
77.58
77.16
76.74
76.28
71.09
66.75
66.45
133.96
133.62
133.25
132.89
128.37
128.16
127.79
126.89
126.43
126.16
125.57
123.51
135
130
125
f1 (ppm)
O
O
4ja
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)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6.79
6.78
6.68
6.63
6.11
6.09
6.06
6.03
4.28
4.27
4.27
4.26
4.25
4.24
4.23
4.22
4.22
3.89
3.86
3.85
3.83
3.82
3.81
3.80
3.77
3.73
3.69
3.68
3.66
3.65
3.45
3.42
3.41
3.38
O
O
OMe
4ka
1.12
1.04
1.01
0.98
1.00
1.00
1.01
8.53
1.06
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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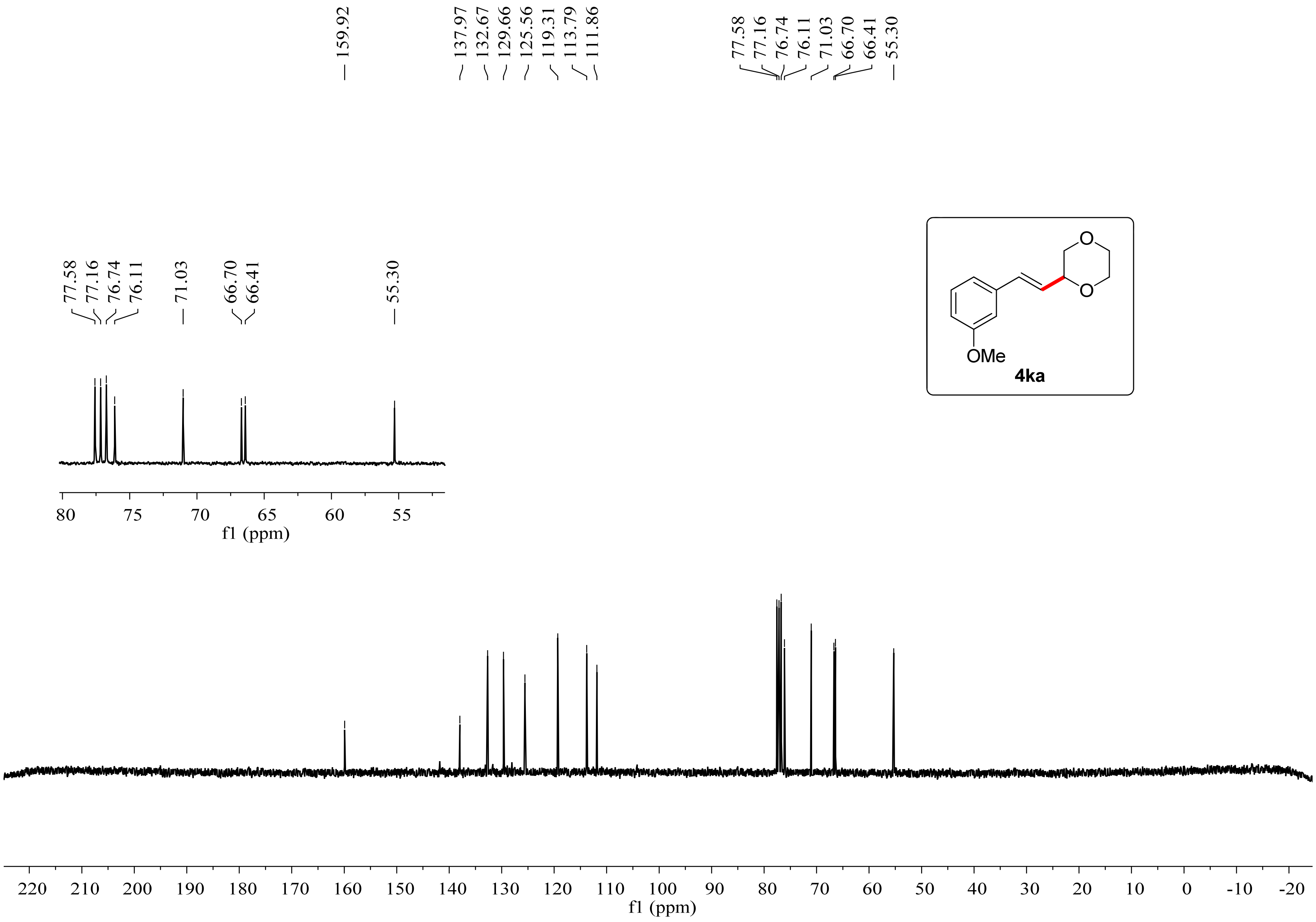
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5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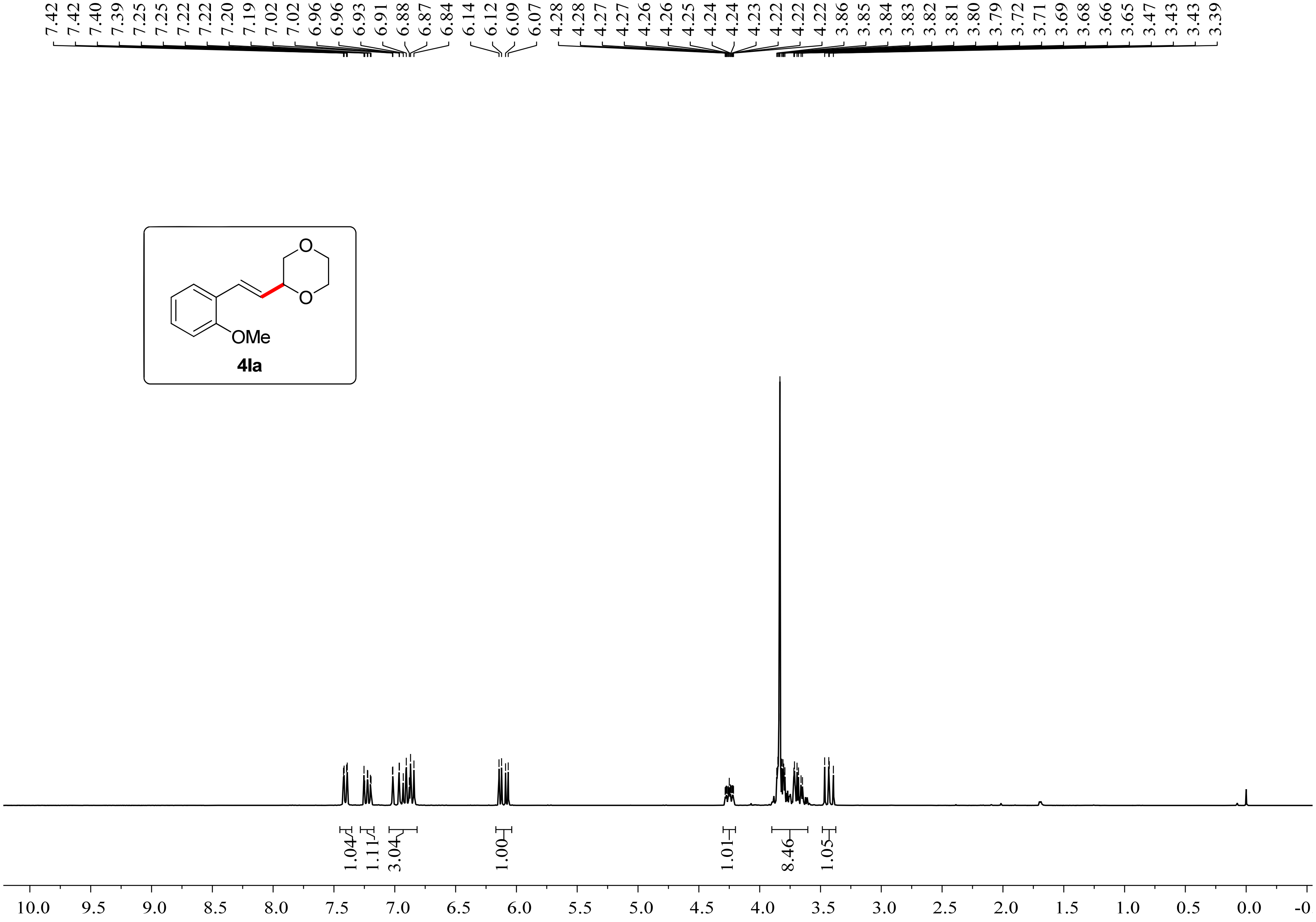
111.86
77.58
77.16
76.74
76.11
71.03
66.70
66.41
55.30
80
75
70
65
60
55
f1 (ppm)
O
O
OMe
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

**4ka**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7.02
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6.96
6.93
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6.88
6.87
6.84
6.14
6.12
6.09
6.07
4.28
4.28
4.27
4.27
4.26
4.26
4.25
4.24
4.24
4.23
4.22
4.22
4.22
3.86
3.85
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3.83
3.82
3.81
3.80
3.79
3.72
3.71
3.69
3.68
3.66
3.65
3.47
3.43
3.43
3.39
O
O
OMe
4la
1.04
1.11
3.04
1.00
1.01
8.46
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9.0
8.5
8.0
7.5
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6.5
6.0
5.5
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4.0
3.5
3.0
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1.5
1.0
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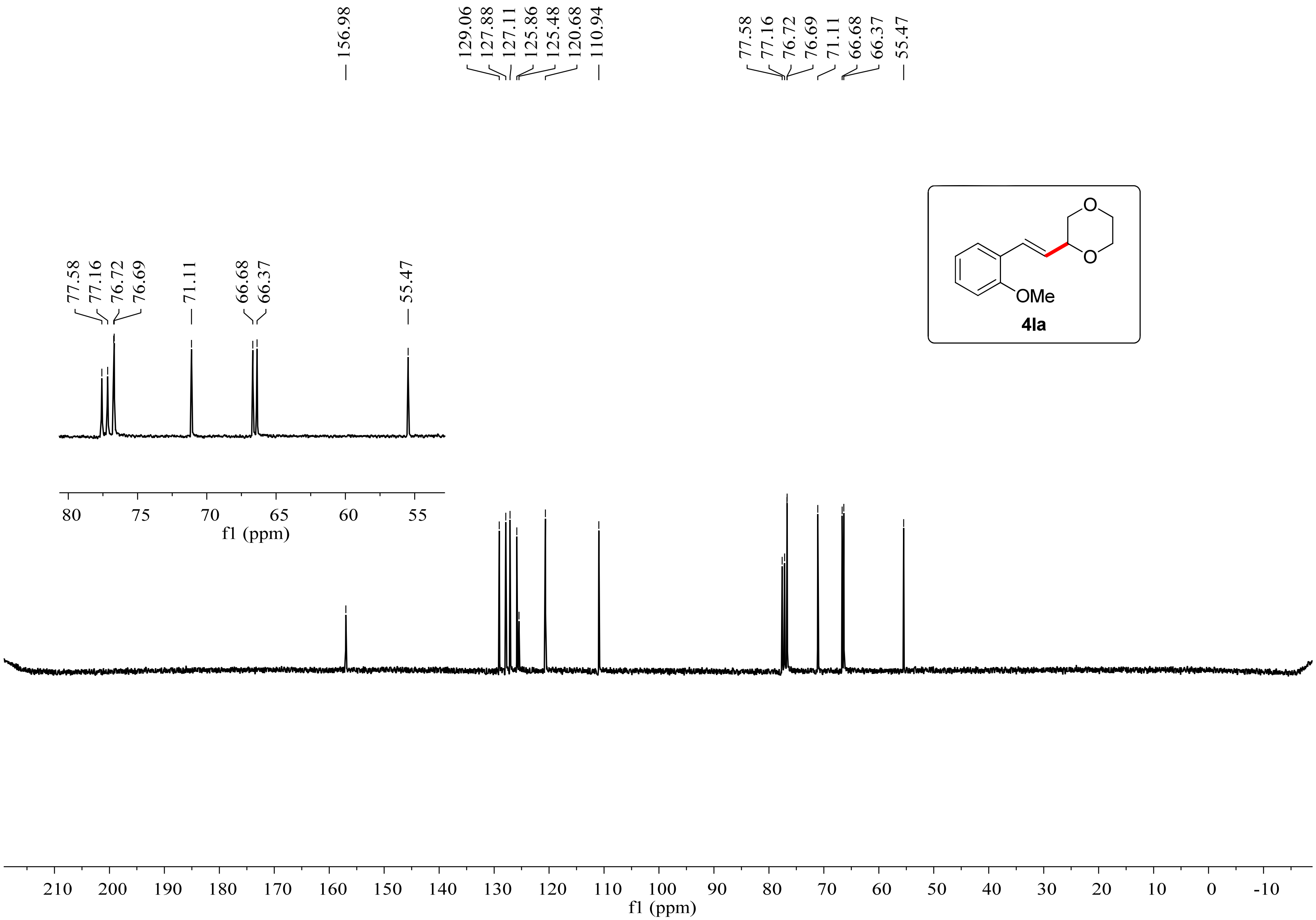
0.0
-0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127.11
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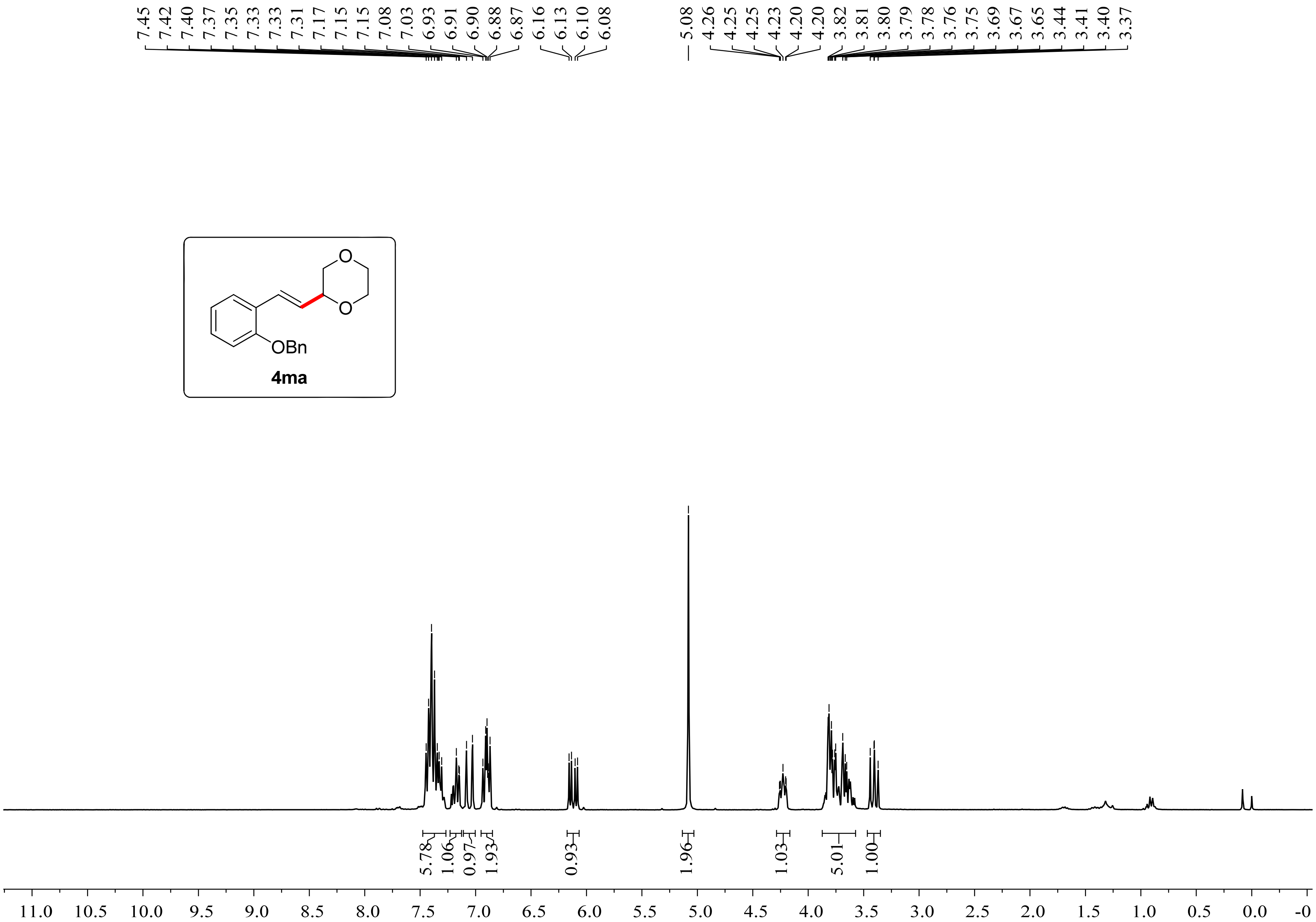
125.48
120.68
110.94
77.58
77.16
76.72
76.69
71.11
66.68
66.37
55.47
80
75
70
65
60
55
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
O
O
OMe
4la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6.91
6.90
6.88
6.87
6.16
6.13
6.10
6.08
5.08
4.26
4.25
4.25
4.23
4.20
4.20
3.82
3.81
3.80
3.79
3.78
3.76
3.75
3.69
3.67
3.65
3.44
3.41
3.40
3.37
O
O
OBn
4ma
5.78
1.06
0.97
1.93
0.93
1.96
1.03
5.01
1.00
11.0
10.5
10.0
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9.0
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7.0
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6.0
5.5
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1.5
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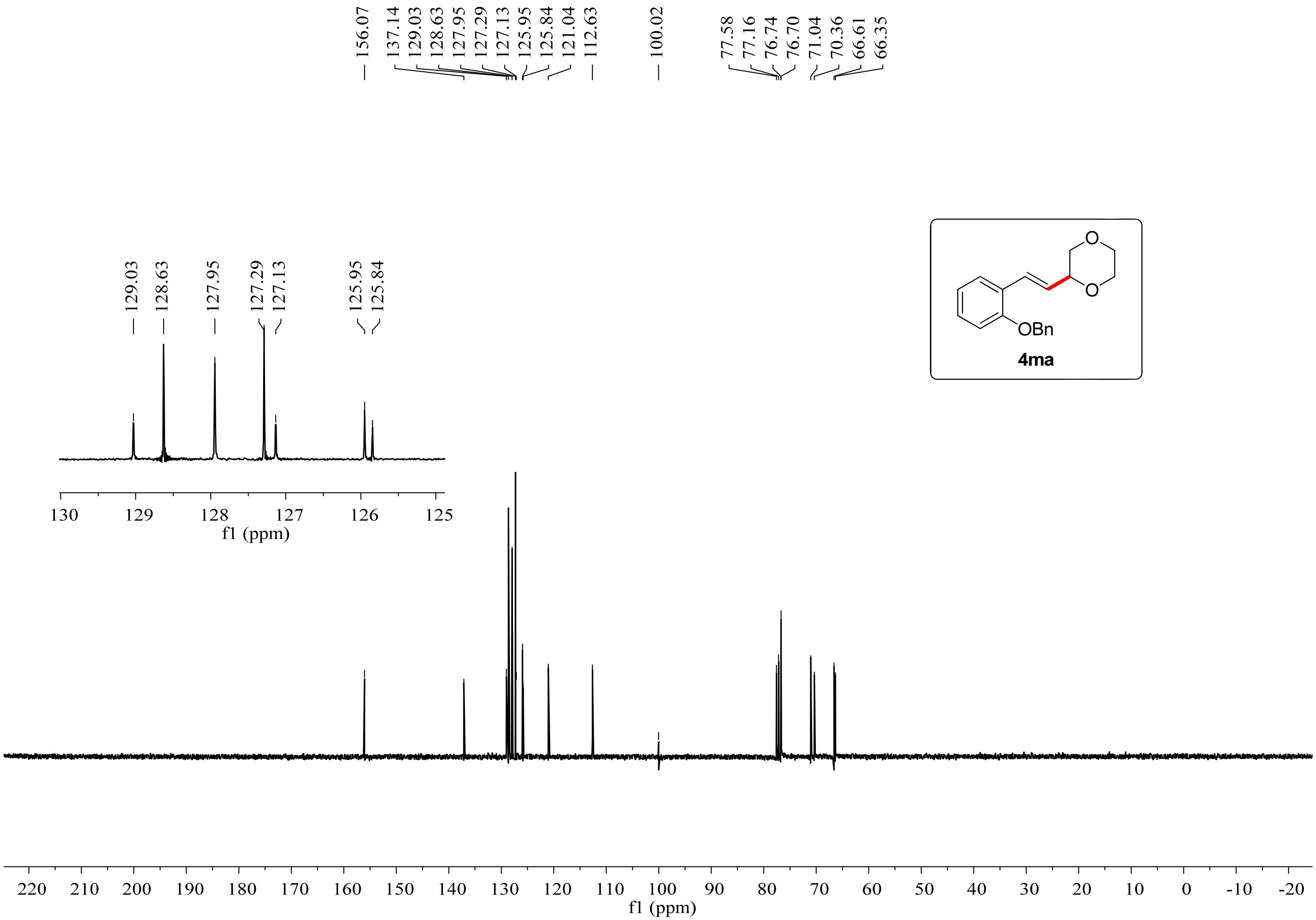
0.0
-0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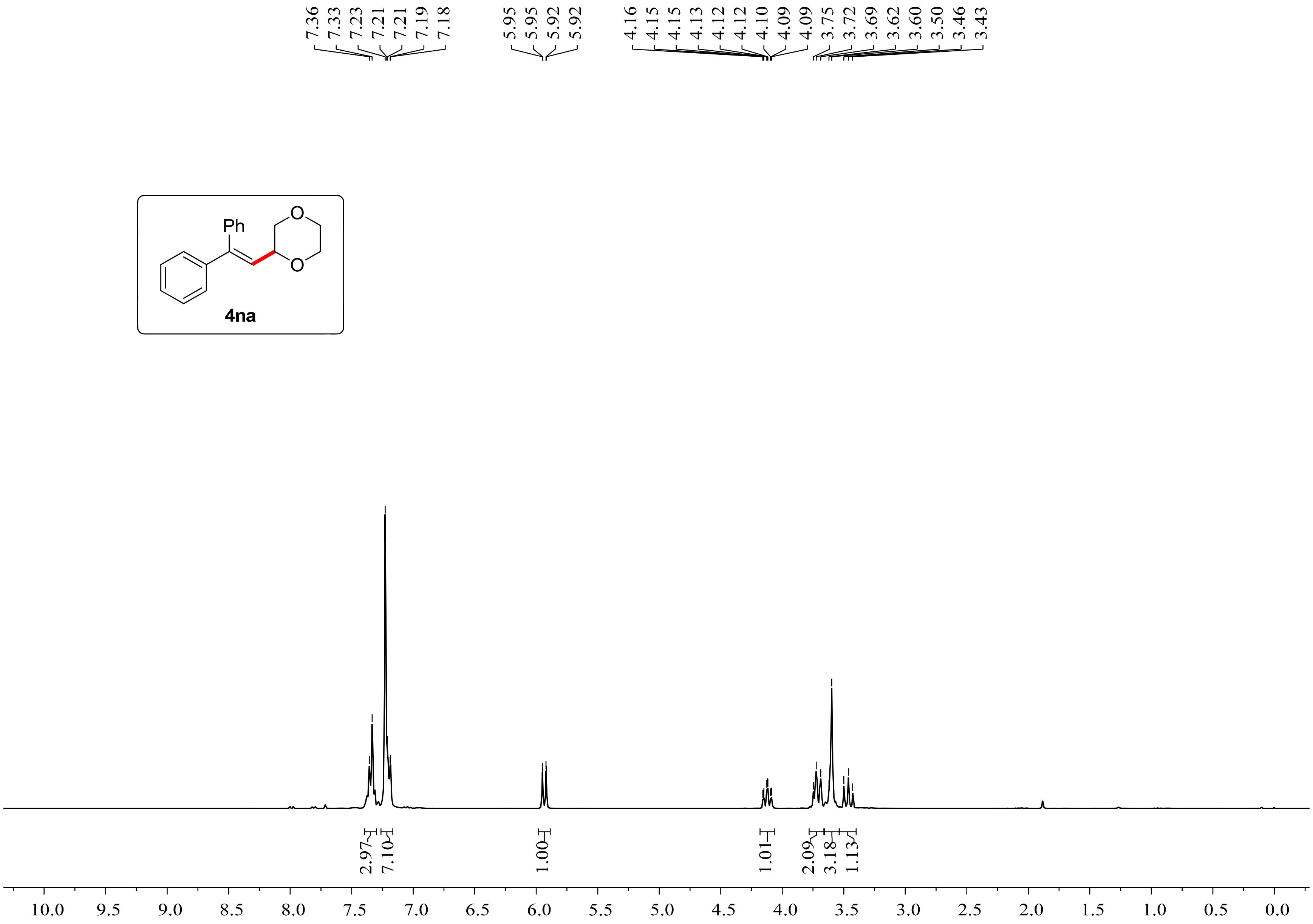
100.02
77.58
77.16
76.74
76.70
71.04
70.36
66.61
66.35
129.03
128.63
127.95
127.29
127.13
125.95
125.84
130
129
128
127
126
125
f1 (ppm)
O
O
OBn
4ma
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)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5.92
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4.15
4.15
4.13
4.12
4.12
4.10
4.09
4.09
3.75
3.72
3.69
3.62
3.60
3.50
3.46
3.43
Ph
O
O
4na
2.97
7.10
1.00
1.01
2.09
3.18
1.13
10.0
9.5
9.0
8.5
8.0
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6.0
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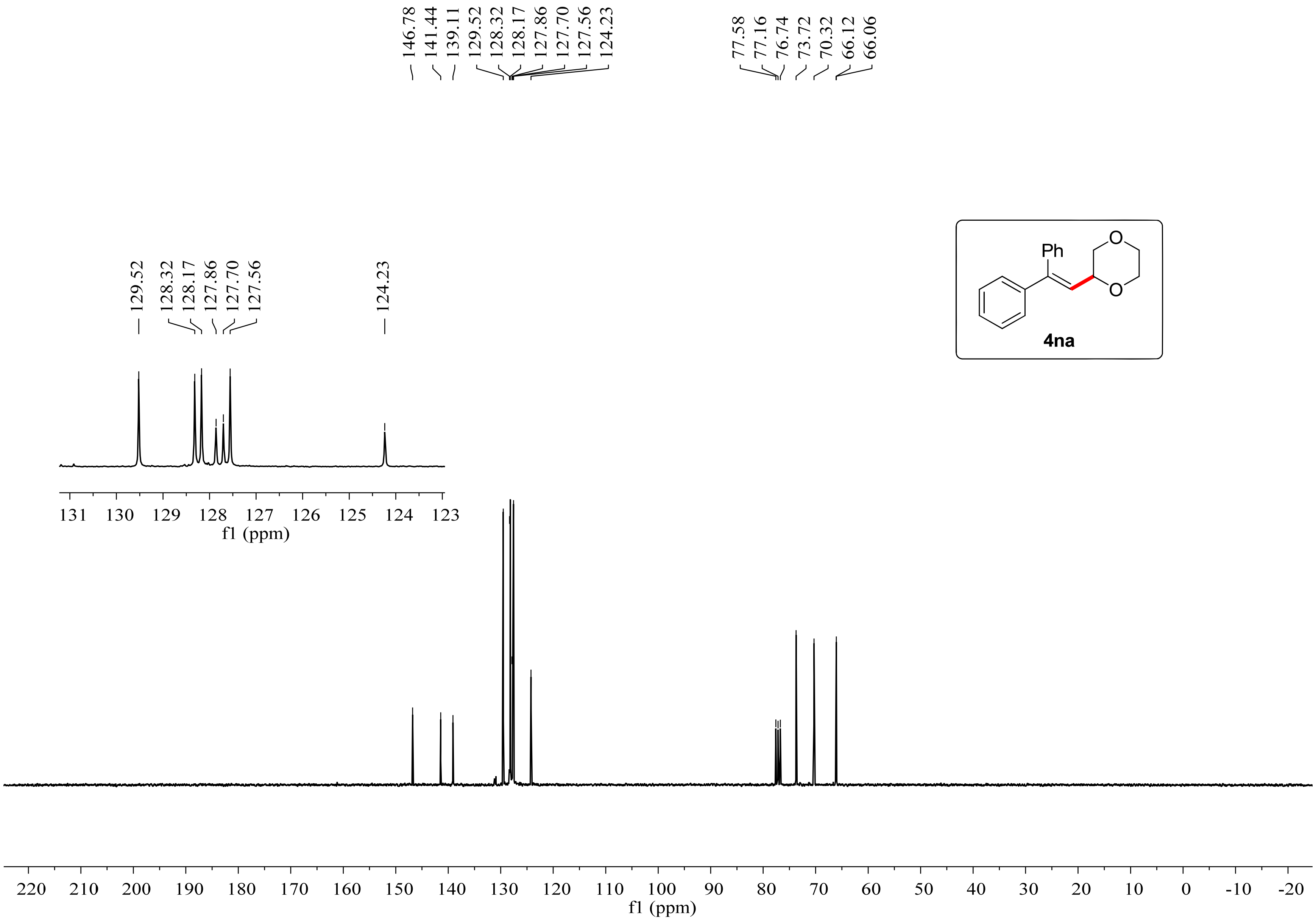
0.0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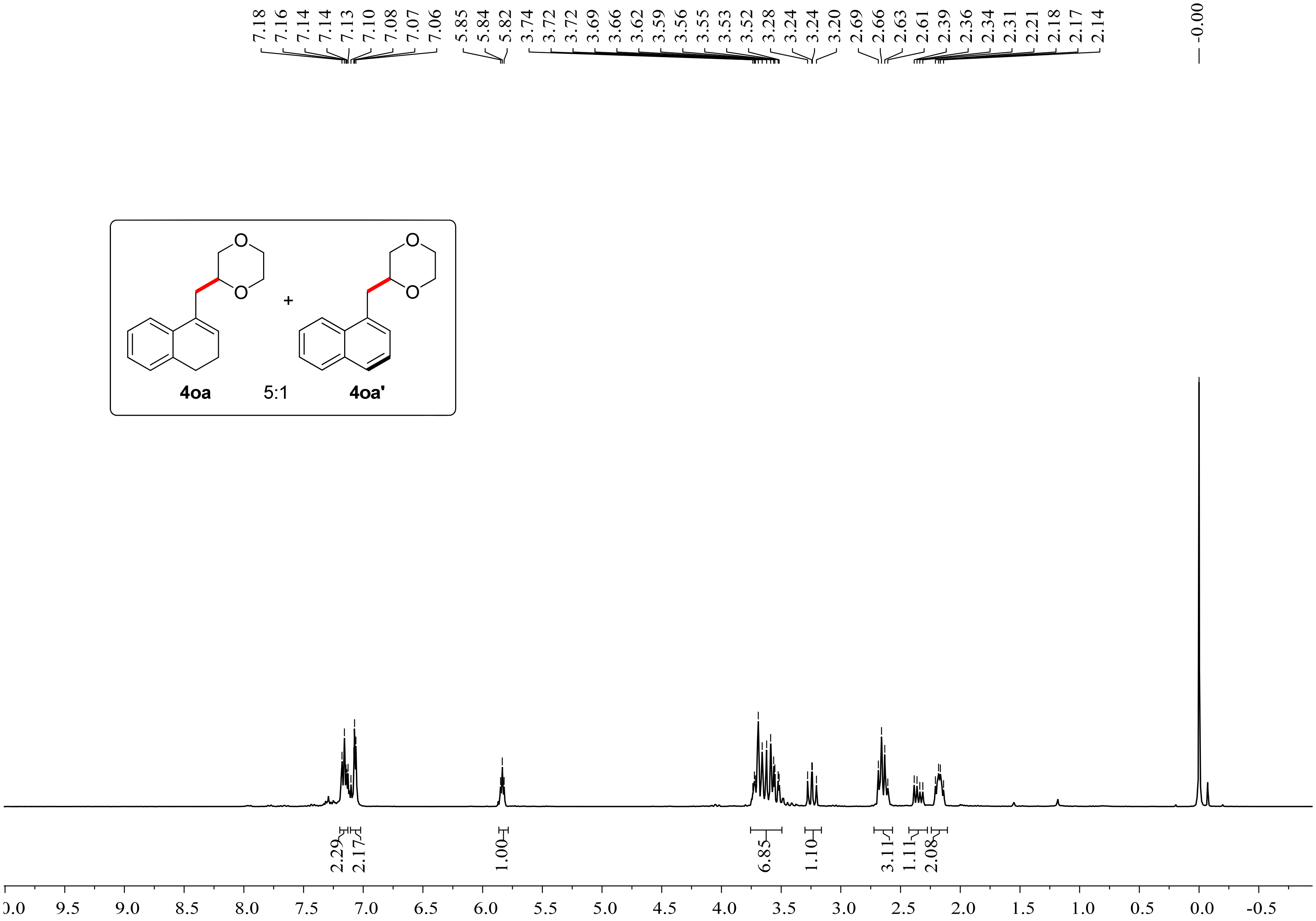
127.56
124.23
77.58
77.16
76.74
73.72
70.32
66.12
66.06
Ph
O
O
4na
129.52
128.32
128.17
127.86
127.70
127.56
124.23
131 130 129 128 127 126 125 124 123
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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7.07
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5.82
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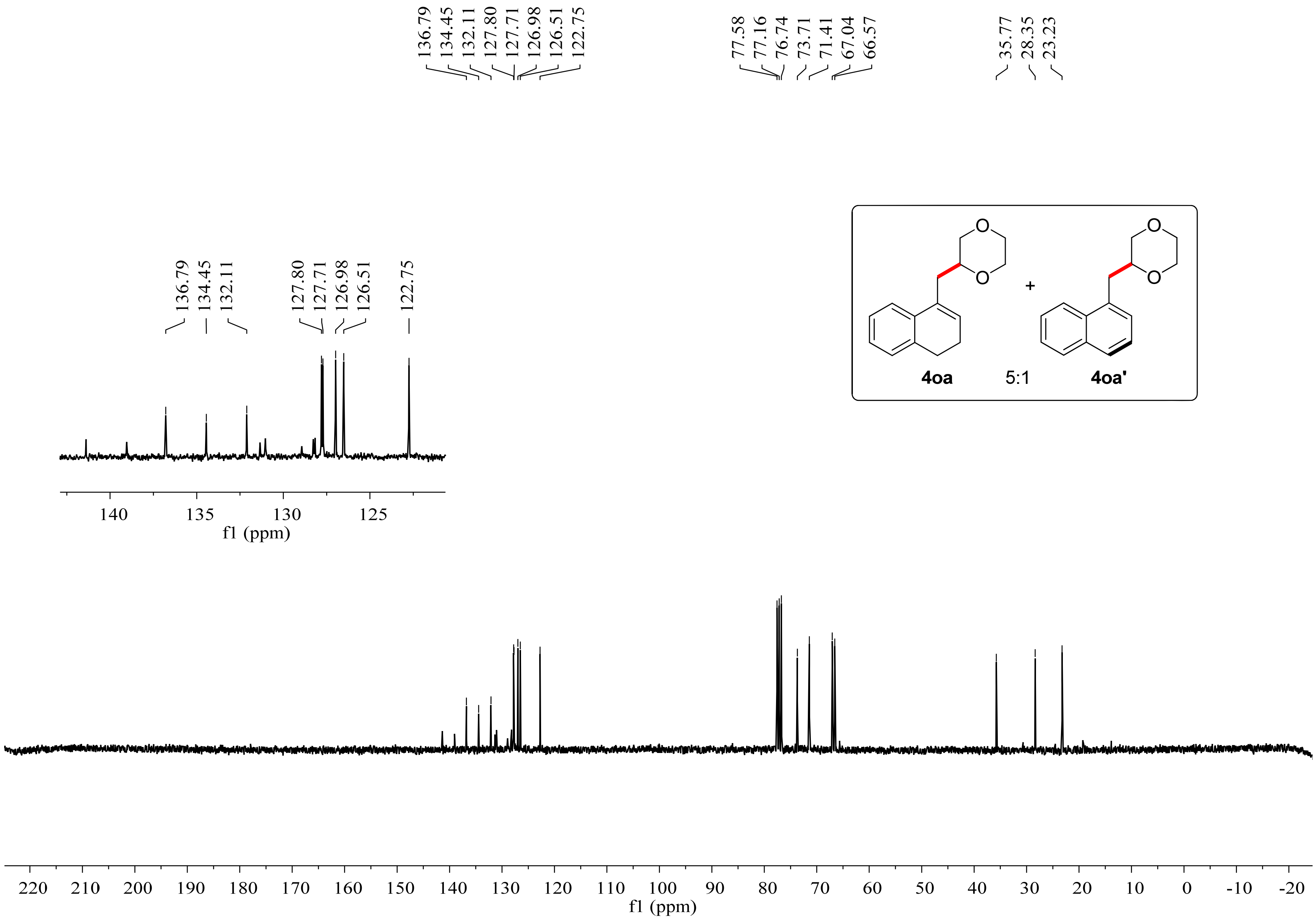
3.72
3.72
3.69
3.66
3.62
3.59
3.56
3.55
3.53
3.52
3.28
3.24
3.24
3.20
2.69
2.66
2.63
2.61
2.39
2.36
2.34
2.31
2.21
2.18
2.17
2.14
-0.00
2.29
2.17
1.00
6.85
1.10
3.11
1.11
2.08
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

O
O
+
O
O

**4oa** 5:1 **4oa'**


136.79
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132.11
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126.98
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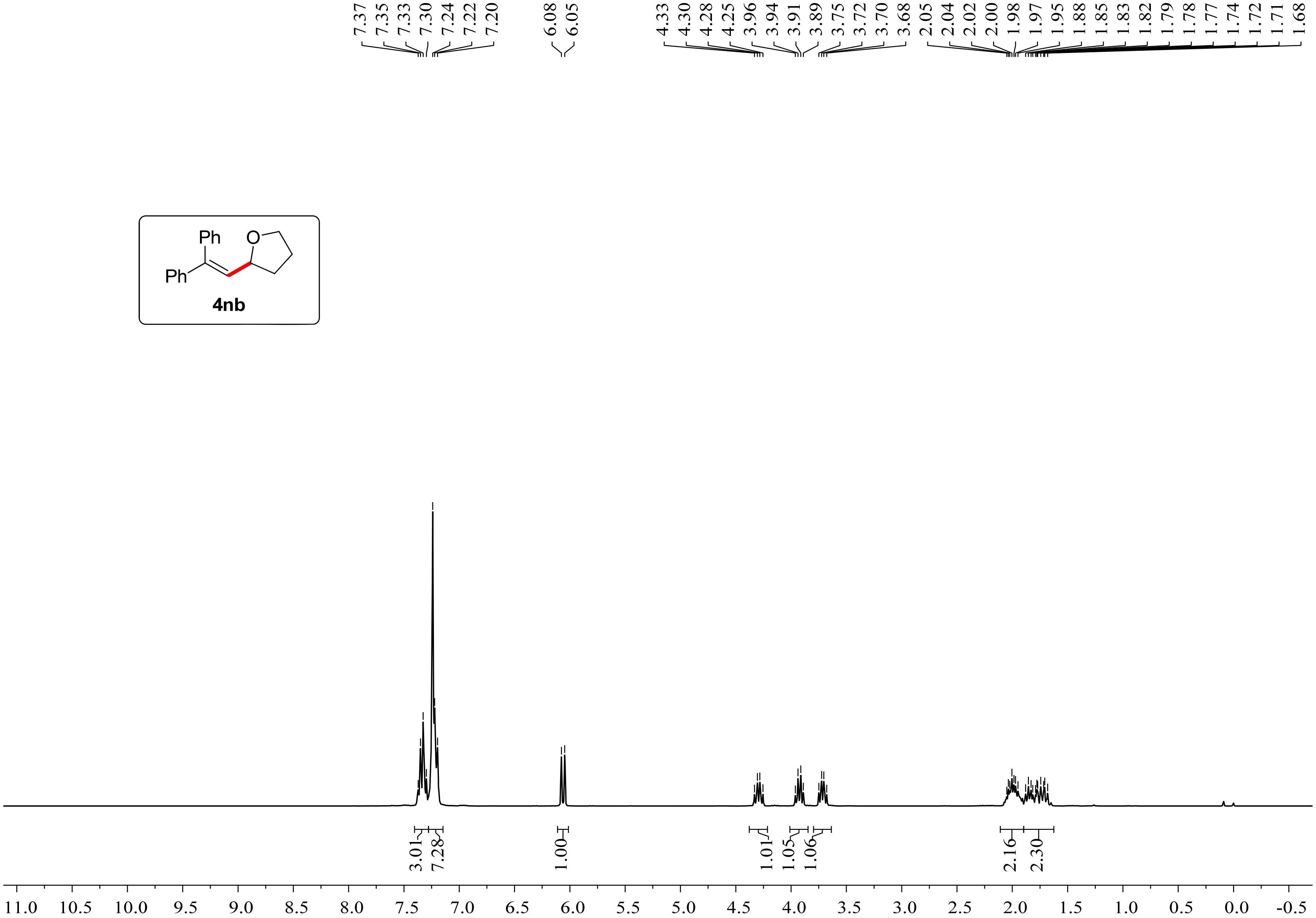
122.75
77.58
77.16
76.74
73.71
71.41
67.04
66.57
35.77
28.35
23.23
136.79
134.45
132.11
127.80
127.71
126.98
126.51
122.75
140
135
130
125
f1 (ppm)
O
O
+
O
O
4oa
5:1
4oa'
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

Ph
O
Ph

**4nb**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4.28
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3.96
3.94
3.91
3.89
3.75
3.72
3.70
3.68
2.05
2.04
2.02
2.00
1.98
1.97
1.95
1.88
1.85
1.83
1.82
1.79
1.78
1.77
1.74
1.72
1.71
1.68
3.01
7.28
1.00
1.01
1.05
1.06
2.16
2.30
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10.0
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9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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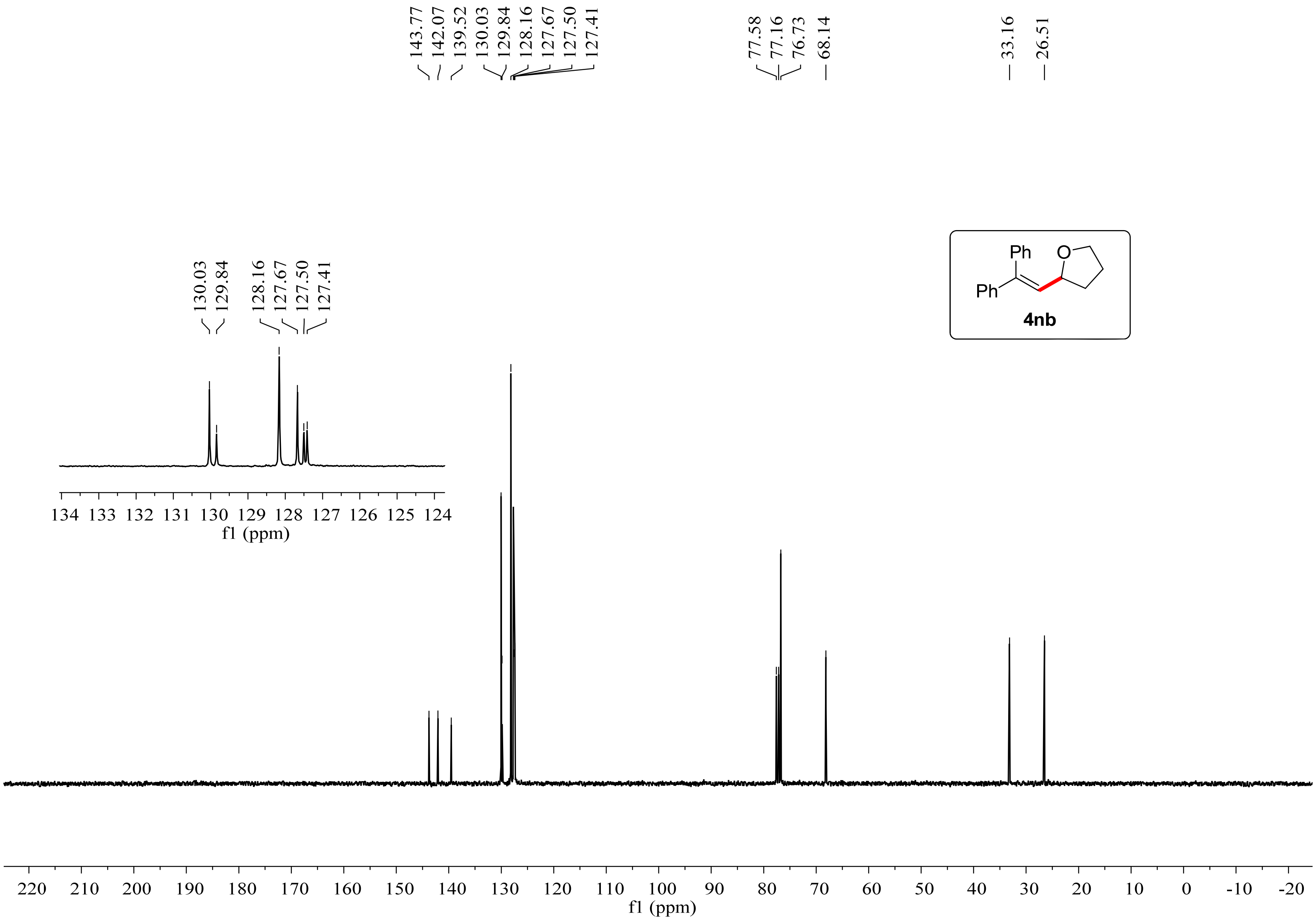
-0.5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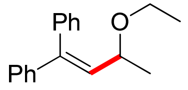
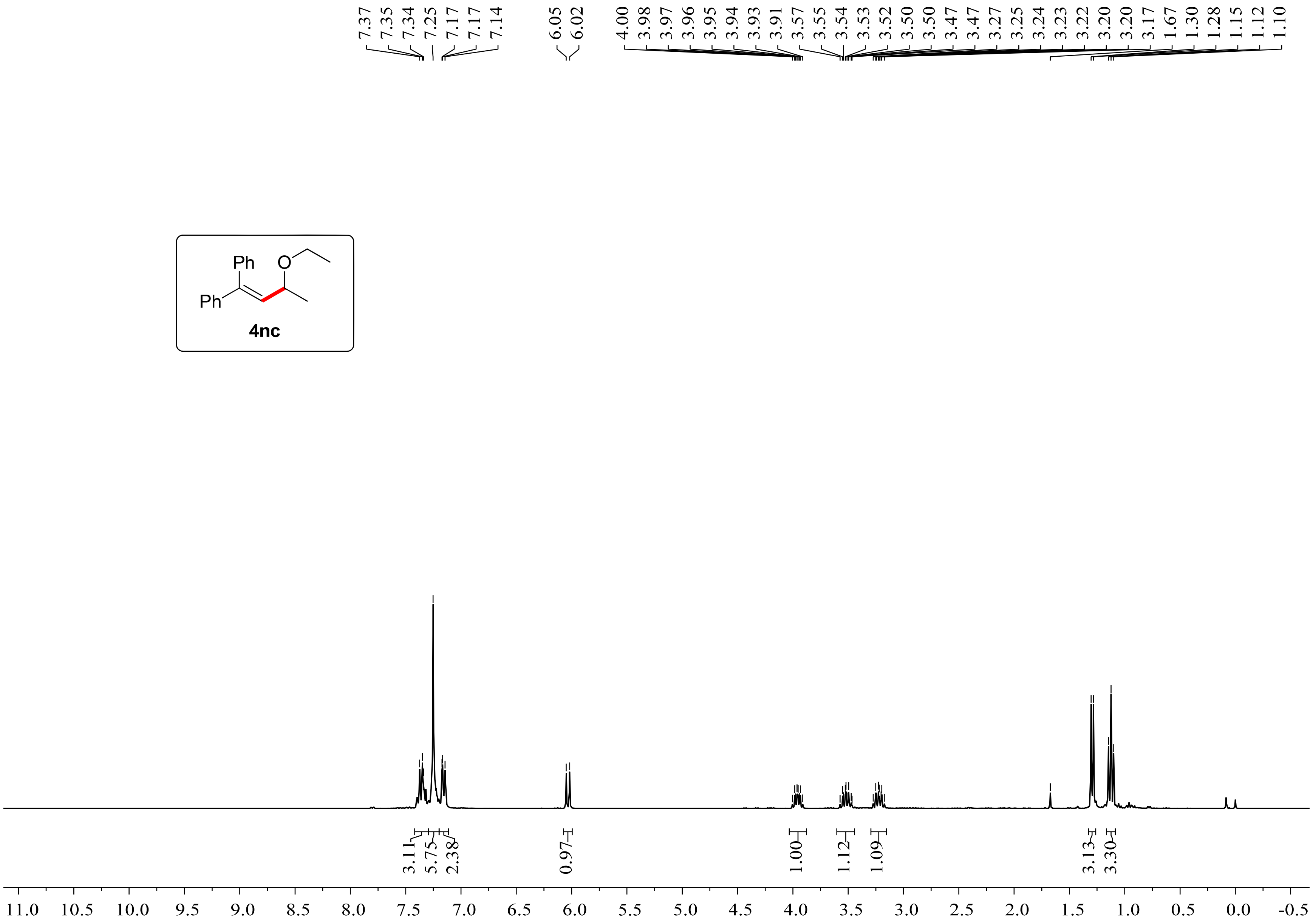
68.14
33.16
26.51
130.03
129.84
128.16
127.67
127.50
127.41
134 133 132 131 130 129 128 127 126 125 124
f1 (ppm)
Ph
O
Ph
4nb
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


Ph
O
Ph

**4nc**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3.97
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3.94
3.93
3.91
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3.54
3.53
3.52
3.50
3.50
3.47
3.47
3.27
3.25
3.24
3.23
3.22
3.20
3.20
3.17
1.67
1.30
1.28
1.15
1.12
1.10
3.11
5.75
2.38
0.97
1.00
1.12
1.09
3.13
3.30
11.0
10.5
10.0
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9.0
8.5
8.0
7.5
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6.5
6.0
5.5
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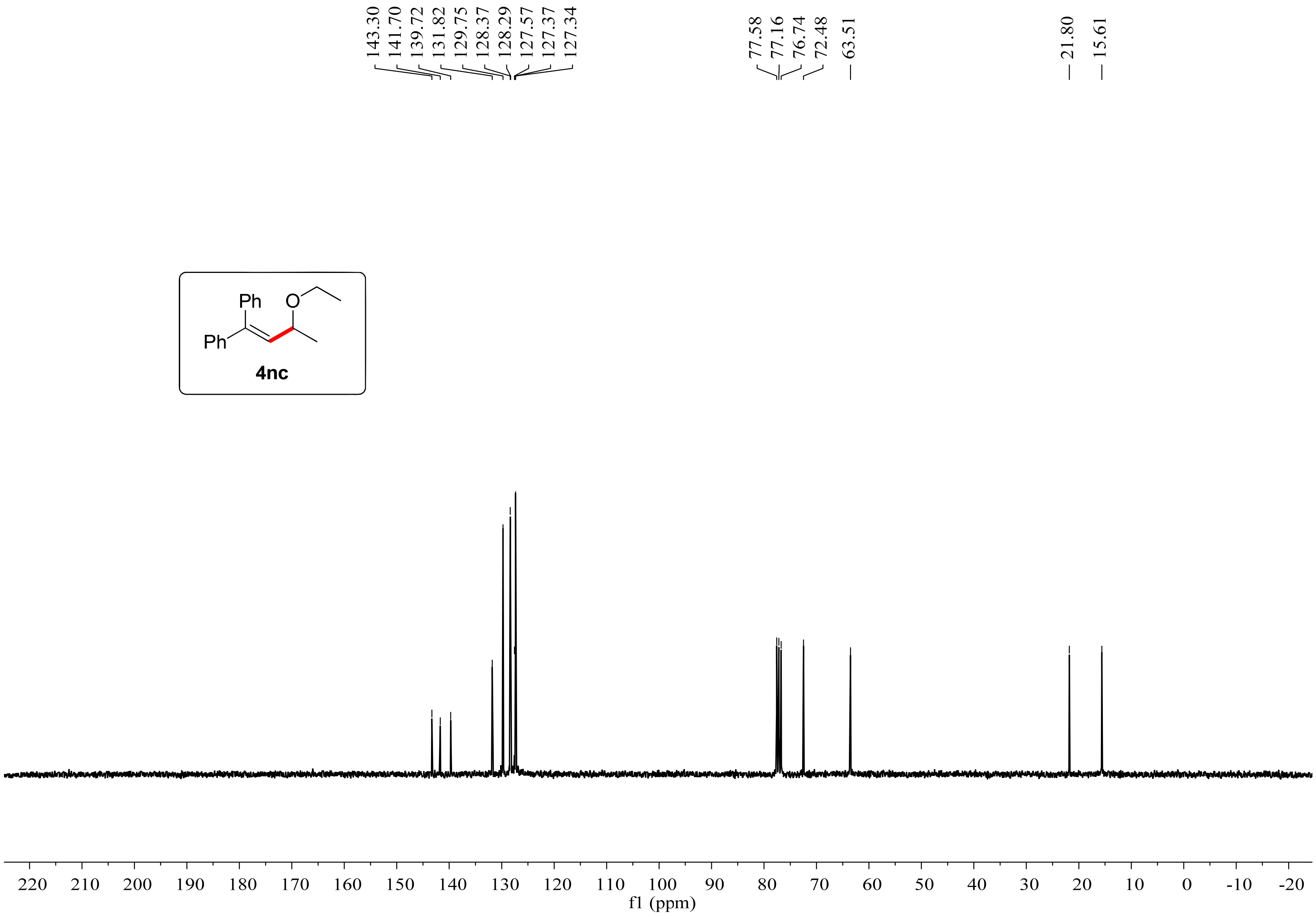

**4nc**

143.30
141.70
139.72
131.82
129.75
128.37
128.29
127.57
127.37
127.34
77.58
77.16
76.74
72.48
63.51
21.80
15.61
220
210
200
190
180
170
160
150
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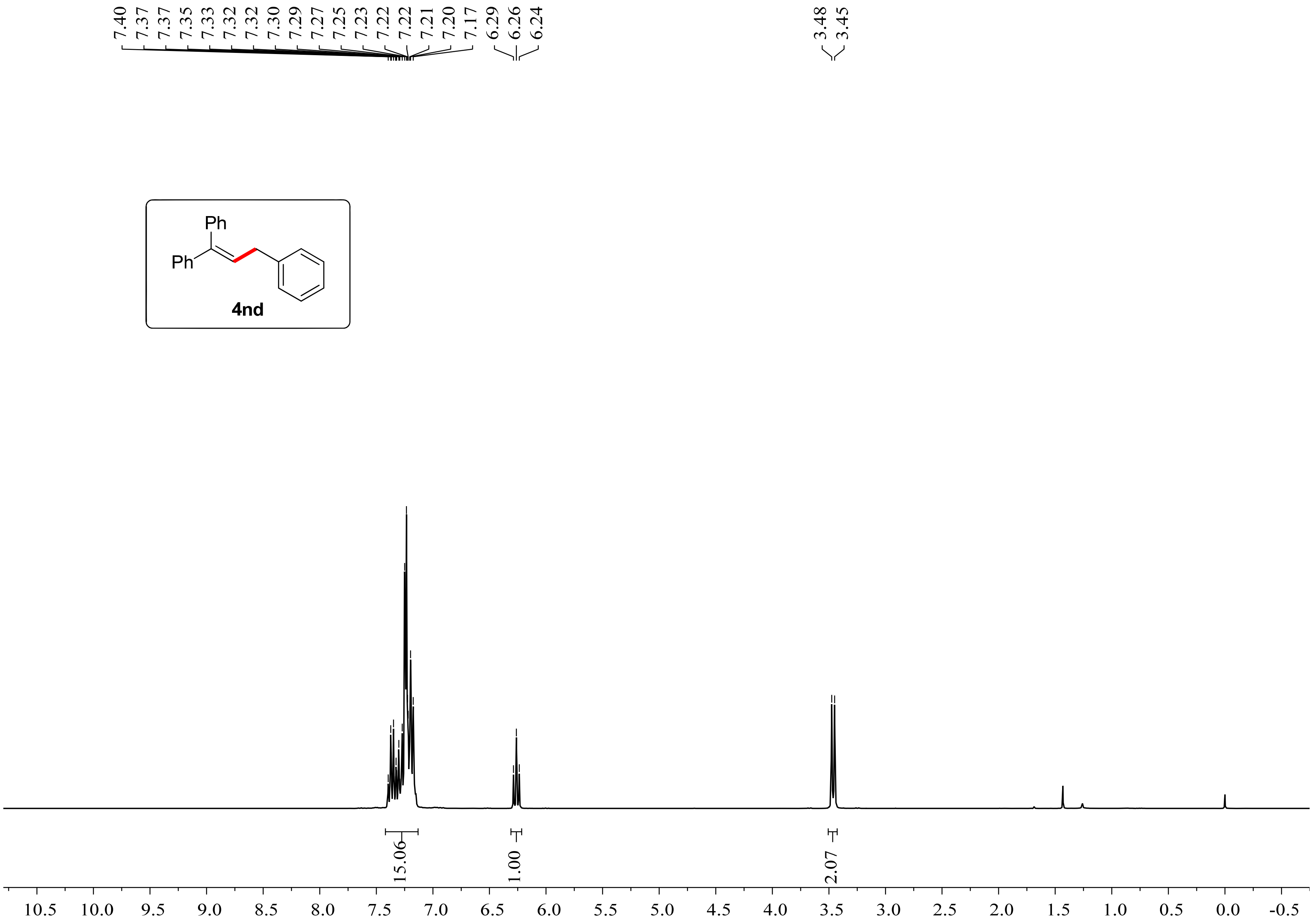
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)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7.22
7.22
7.22
7.21
7.20
7.17
6.29
6.26
6.24
3.48
3.45
Ph
Ph
4nd
15.06
1.00
2.07
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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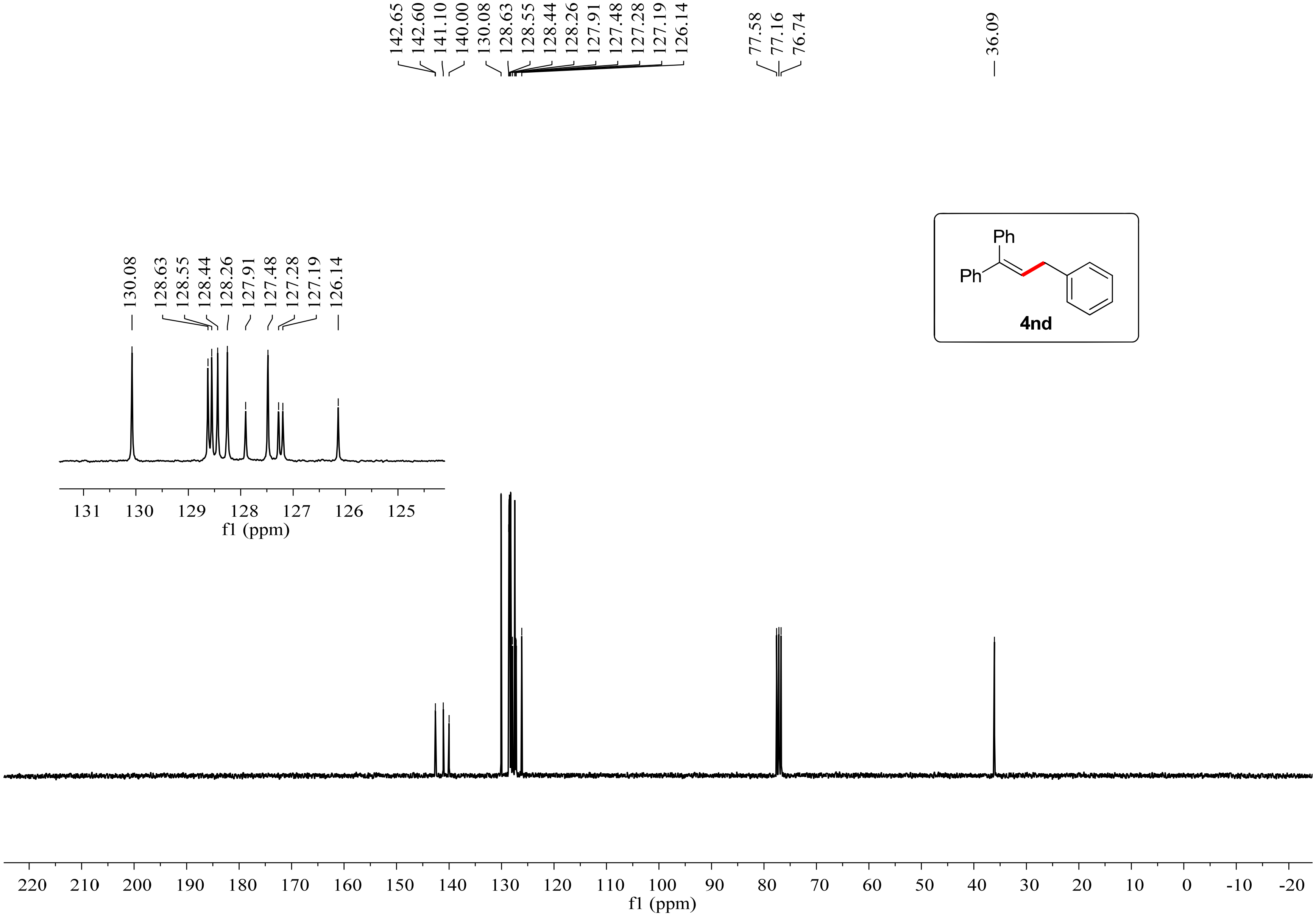
0.0
-0.5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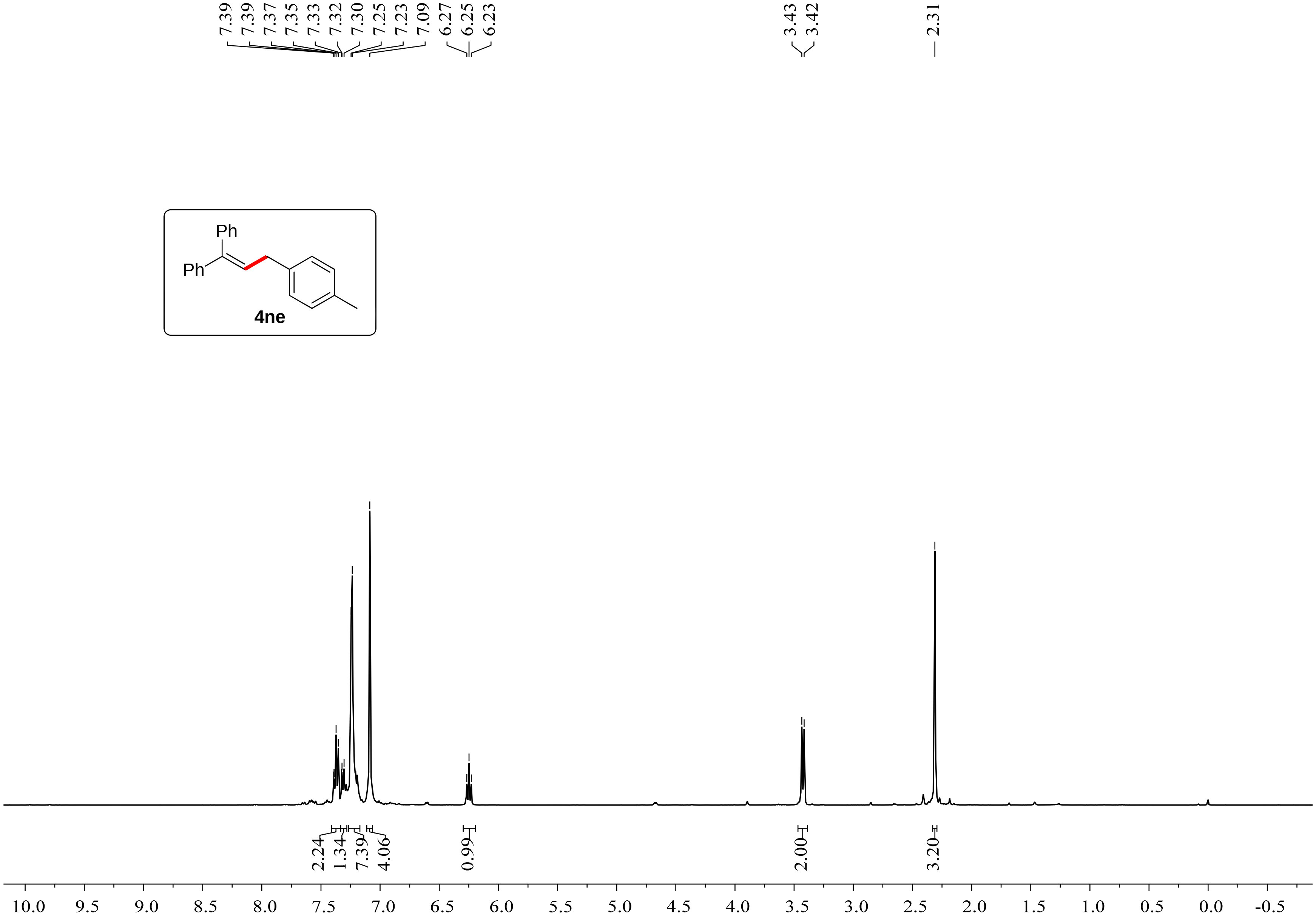
127.19
126.14
77.58
77.16
76.74
36.09
130.08
128.63
128.55
128.44
128.26
127.91
127.48
127.28
127.19
126.14
131
130
129
128
127
126
125
f1 (ppm)
Ph
Ph
4nd
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


**4ne**

7.39
7.39
7.37
7.35
7.33
7.32
7.30
7.25
7.23
7.09
6.27
6.25
6.23
3.43
3.42
2.31
Ph
Ph
2.24
1.34
7.39
4.06
0.99
2.00
3.20
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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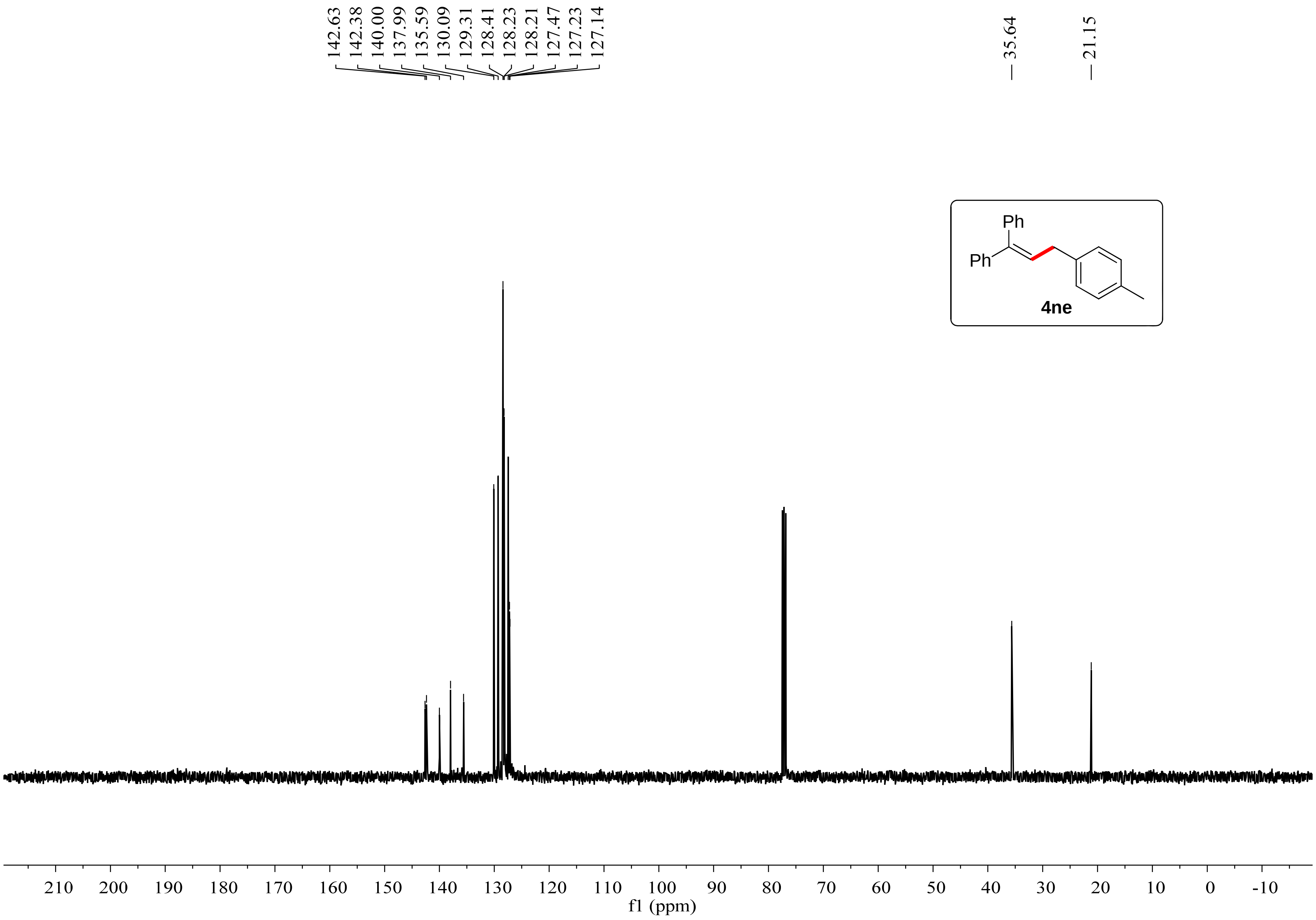
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5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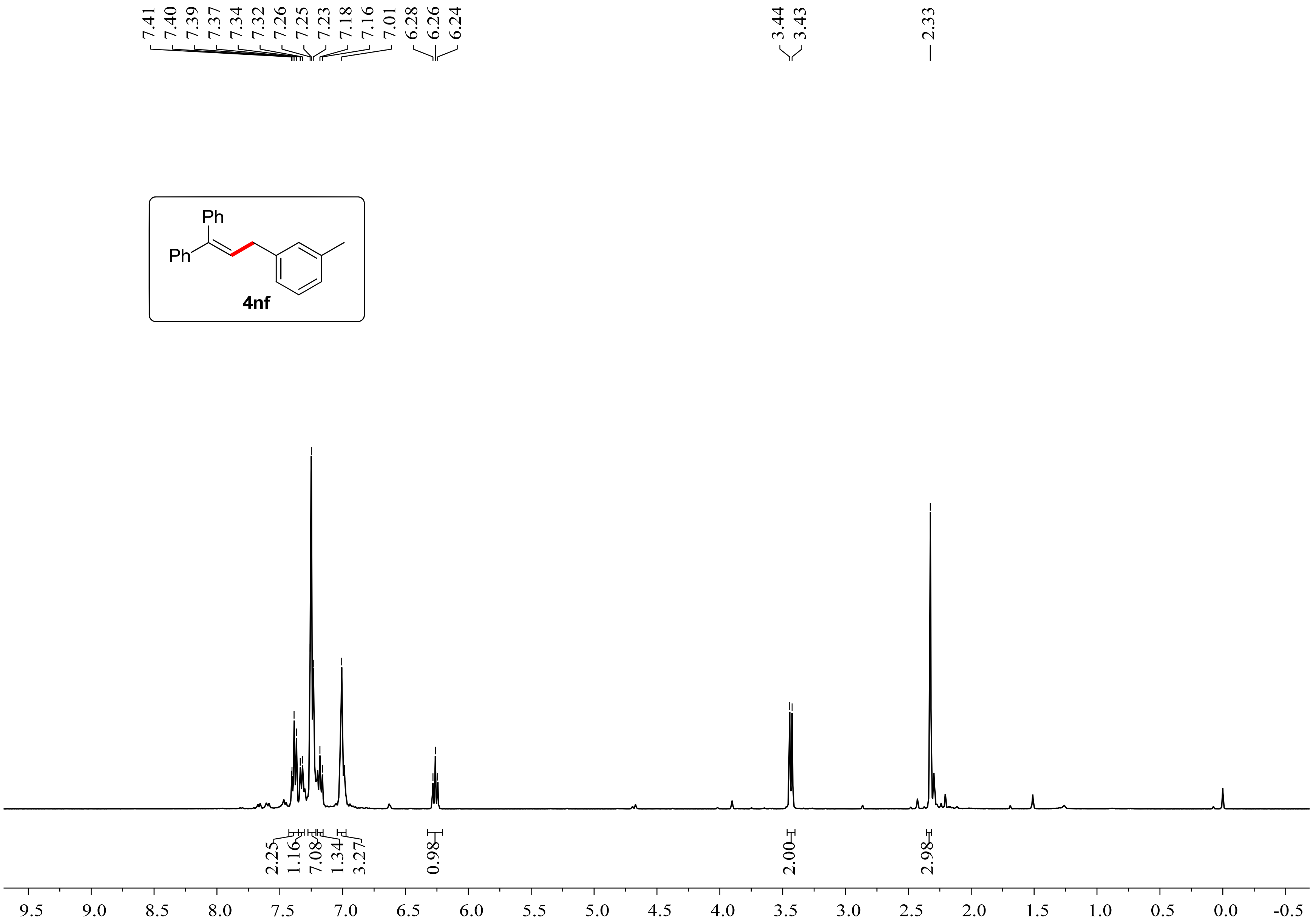
135.59
130.09
129.31
128.41
128.23
128.21
127.47
127.23
127.14
35.64
21.15
Ph
Ph
4ne
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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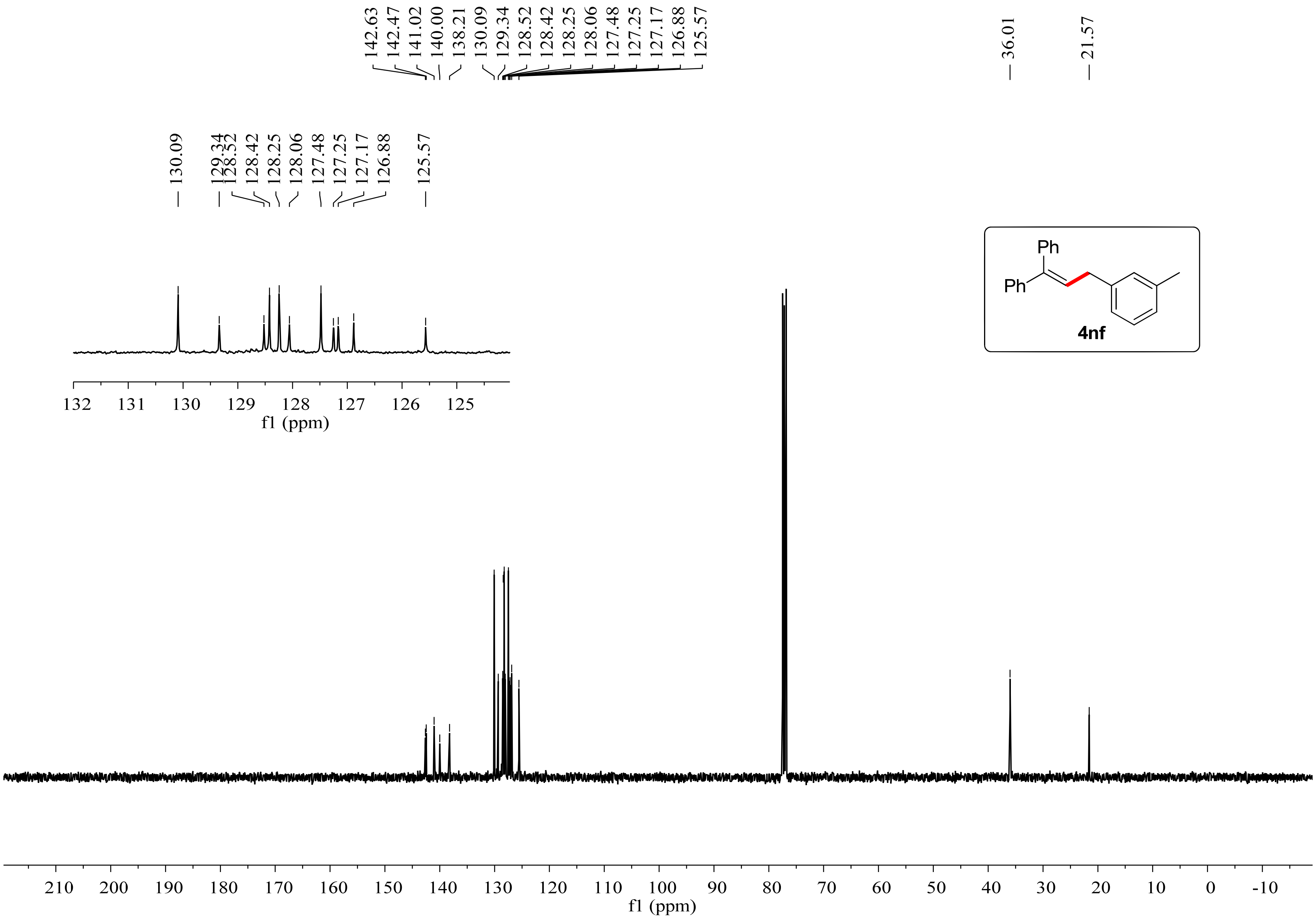
7.32
7.26
7.25
7.23
7.18
7.16
7.01
6.28
6.26
6.24
3.44
3.43
2.33
Ph
Ph
4nf
2.25
1.16
7.08
1.34
3.27
0.98
2.00
2.98
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5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138.21
130.09
129.34
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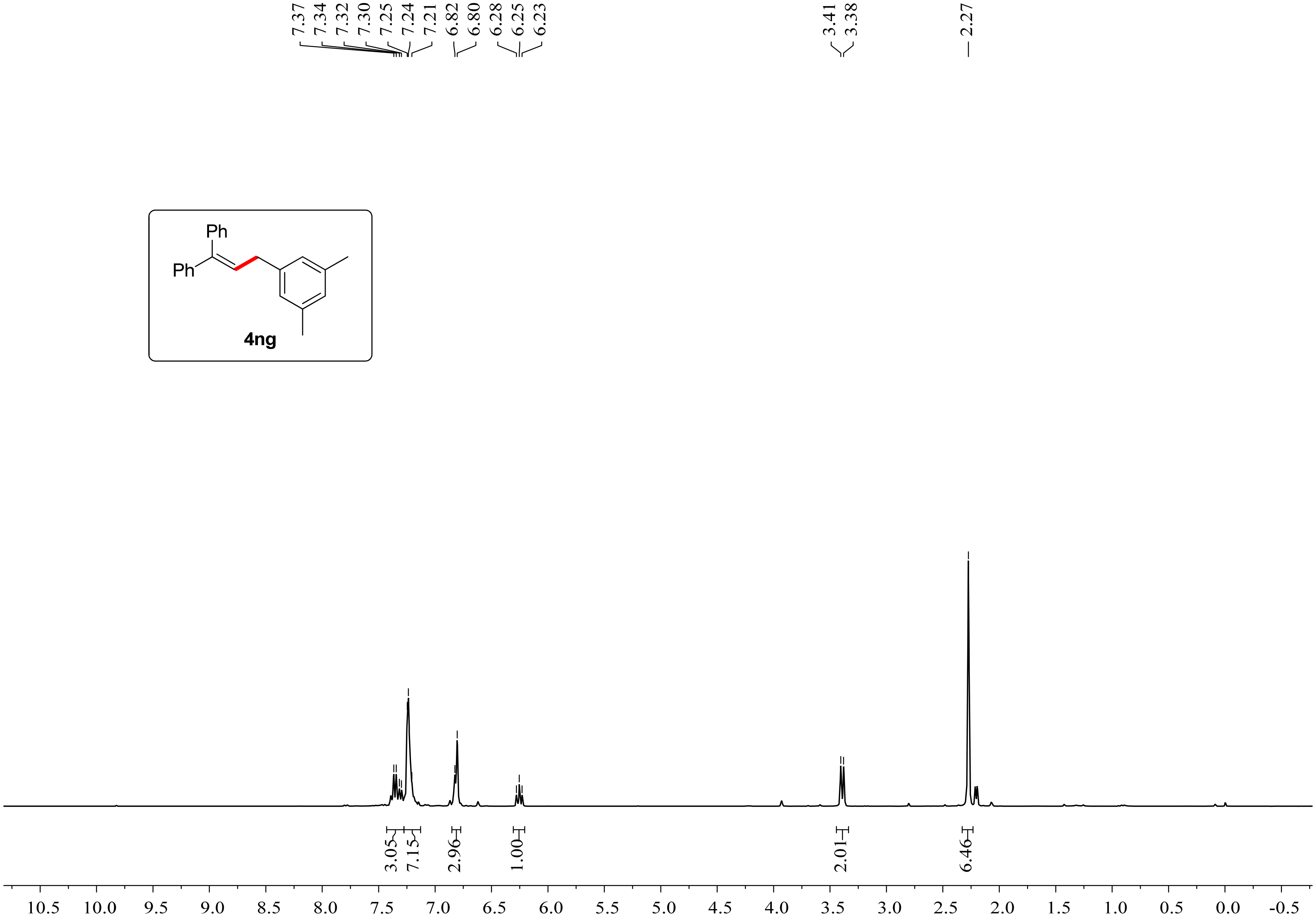
128.25
128.06
127.48
127.25
127.17
126.88
125.57
36.01
21.57
130.09
129.34
128.52
128.42
128.25
128.06
127.48
127.25
127.17
126.88
125.57
132
131
130
129
128
127
126
125
f1 (ppm)
Ph
Ph
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

**4nf**


**4ng**

Ph
Ph
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7.34
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7.30
7.25
7.24
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6.82
6.80
6.28
6.25
6.23
3.41
3.38
2.27
3.05
7.15
2.96
1.00
2.01
6.46
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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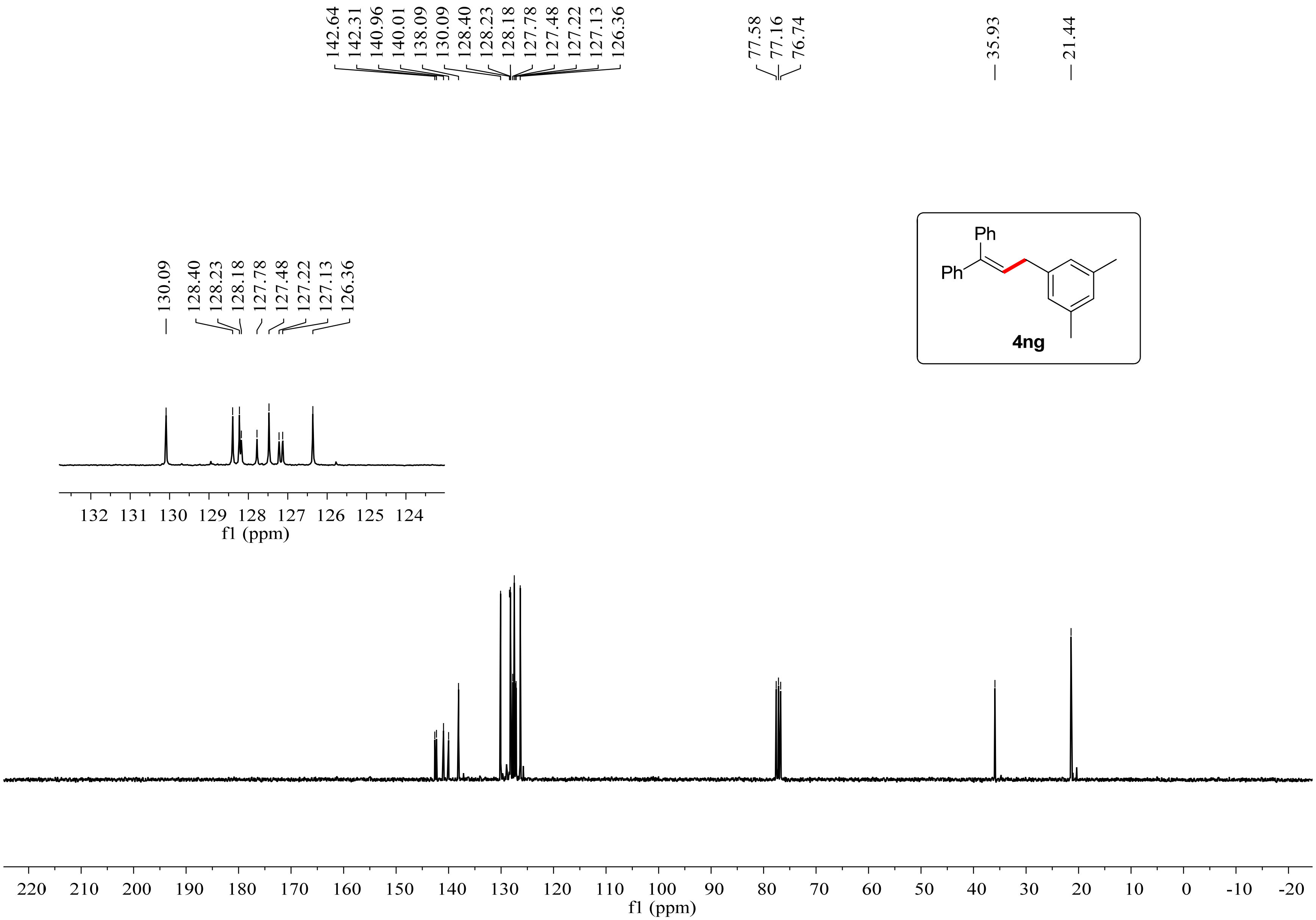
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5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140.01
138.09
130.09
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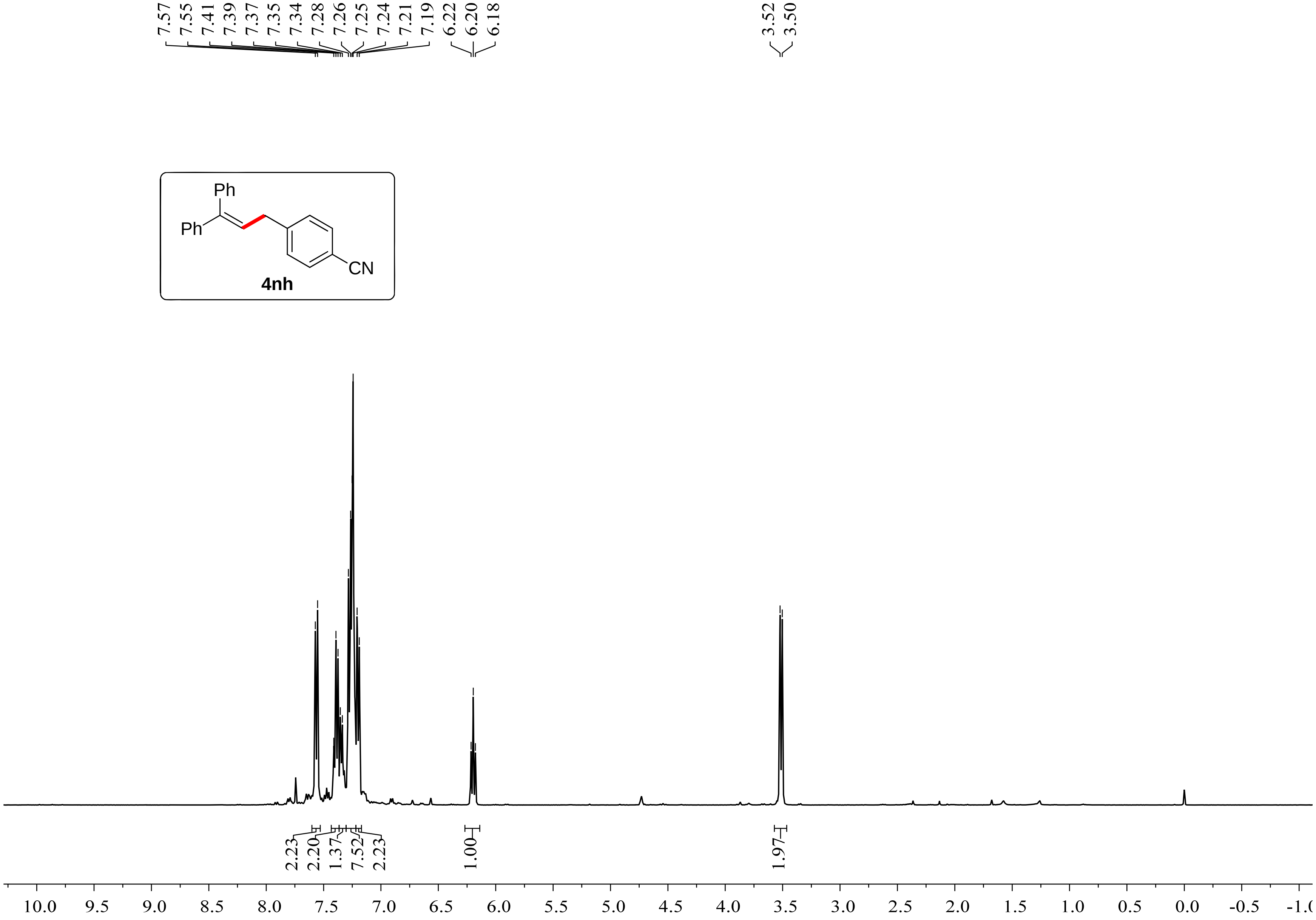
128.23
128.18
127.78
127.48
127.22
127.13
126.36
77.58
77.16
76.74
35.93
21.44
Ph
Ph
132 131 130 129 128 127 126 125 124
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

**4ng**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7.19
6.22
6.20
6.18
3.52
3.50
Ph
Ph
CN
2.23
2.20
1.37
7.52
2.23
1.00
1.97
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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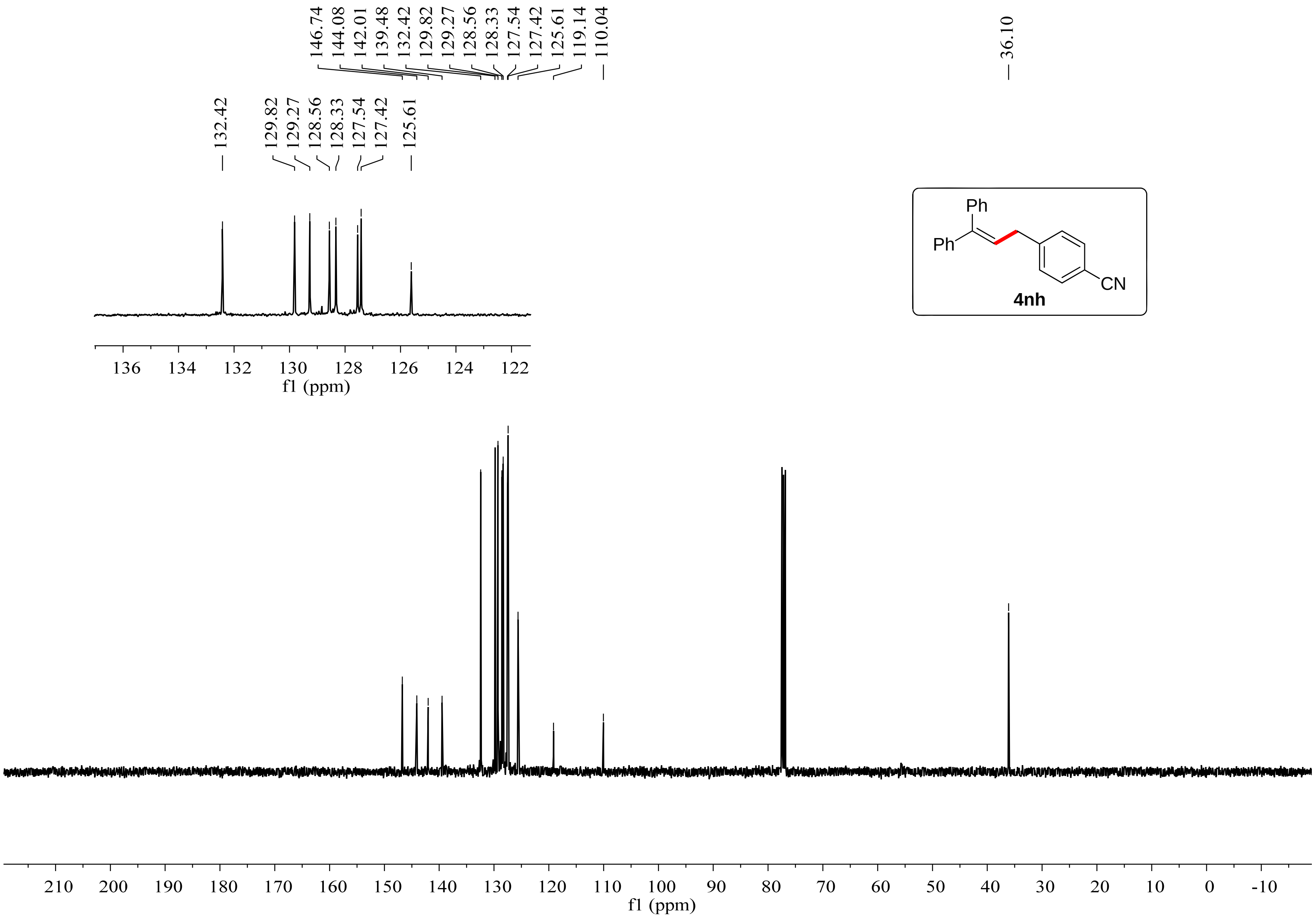
0.0
-0.5
-1.0

**4nh**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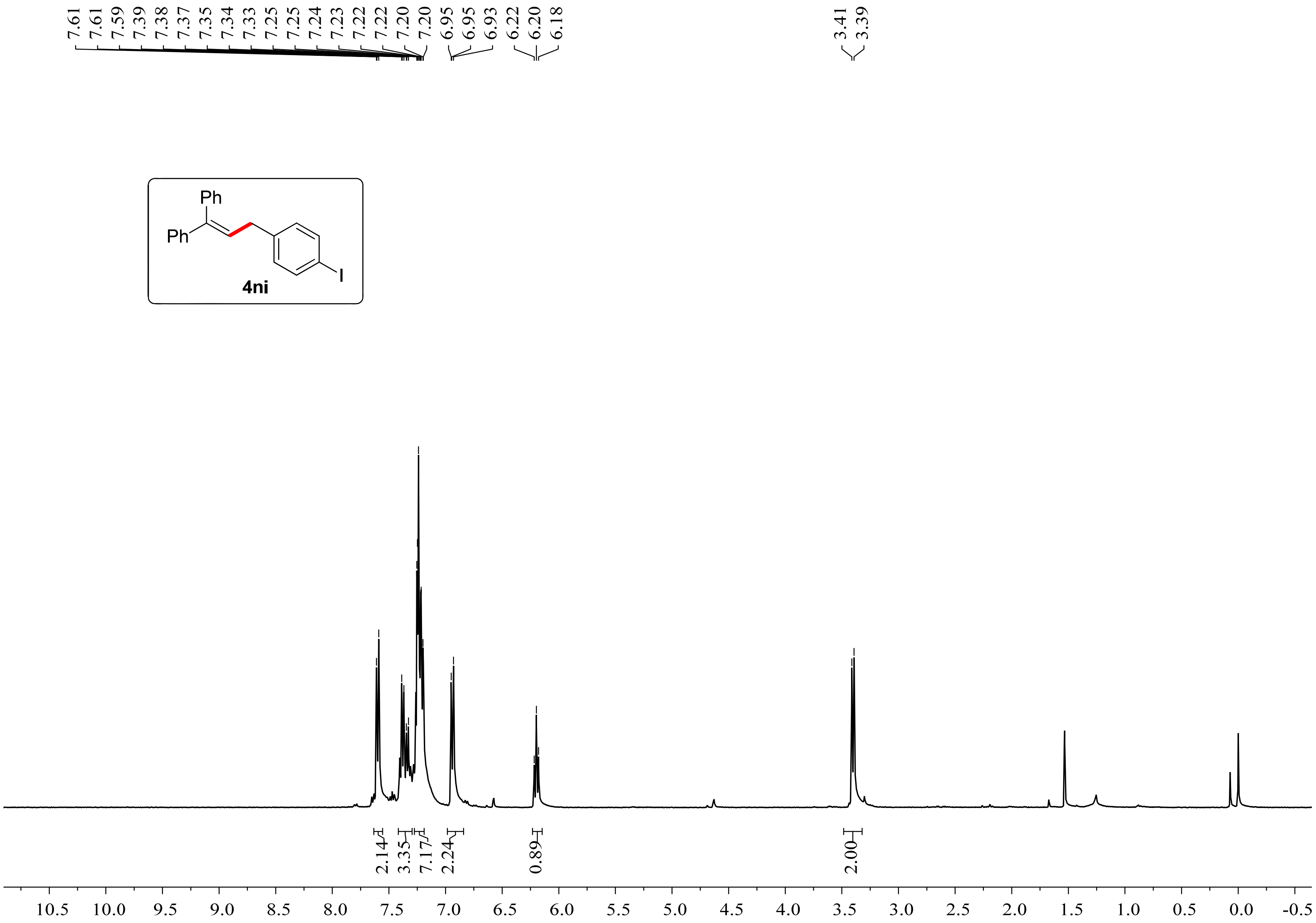
119.14
110.04
36.10
132.42
129.82
129.27
128.56
128.33
127.54
127.42
125.61
136
134
132
130
128
126
124
122
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

Ph
Ph
CN

**4nh**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7.22
7.22
7.20
7.20
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6.95
6.93
6.22
6.20
6.18
3.41
3.39
Ph
Ph
I
4ni
2.14
3.35
7.17
2.24
0.89
2.00
10.5
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9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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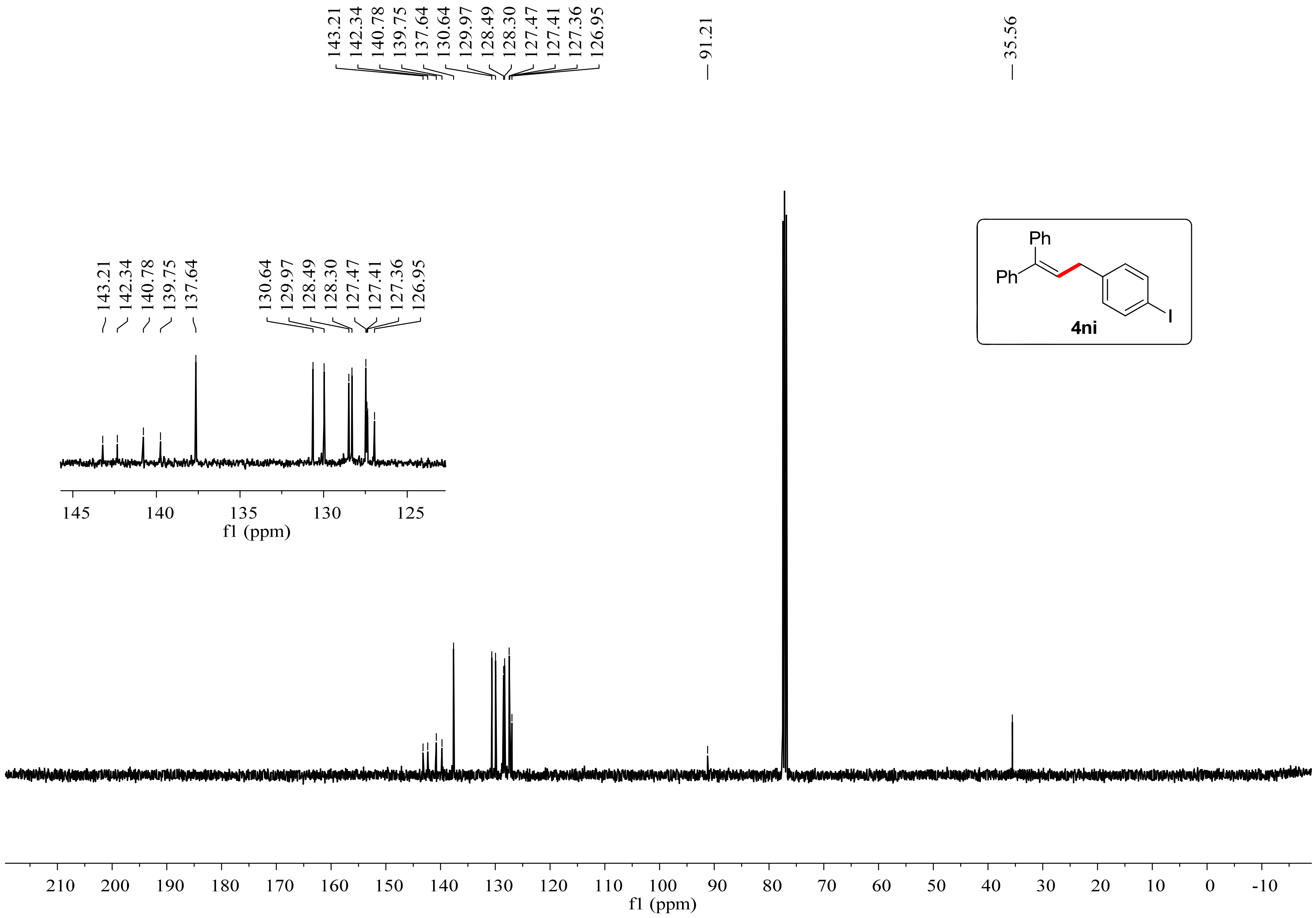
-0.5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127.47
127.41
127.36
126.95
91.21
35.56
Ph
Ph
I
4ni
145
140
135
130
125
f1 (ppm)
210
200
190
180
170
160
150
140
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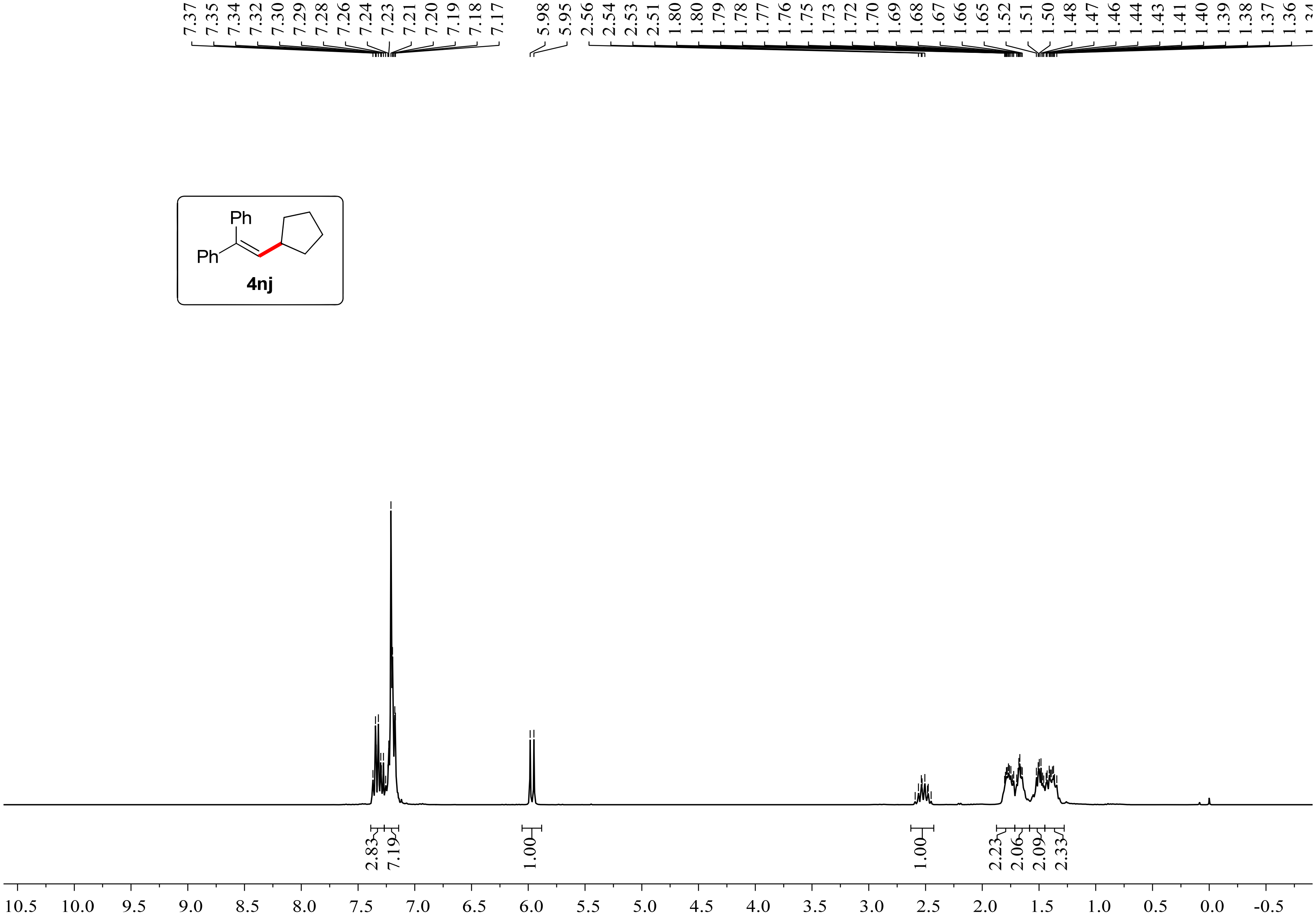
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.19
7.18
7.17
5.98
5.95
2.56
2.54
2.53
2.51
1.80
1.80
1.79
1.78
1.77
1.76
1.75
1.73
1.72
1.70
1.69
1.68
1.67
1.66
1.65
1.52
1.51
1.50
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1.47
1.46
1.44
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1.41
1.40
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1.38
1.37
1.36
Ph
Ph
4nj
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1.00
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2.06
2.09
2.33
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6.5
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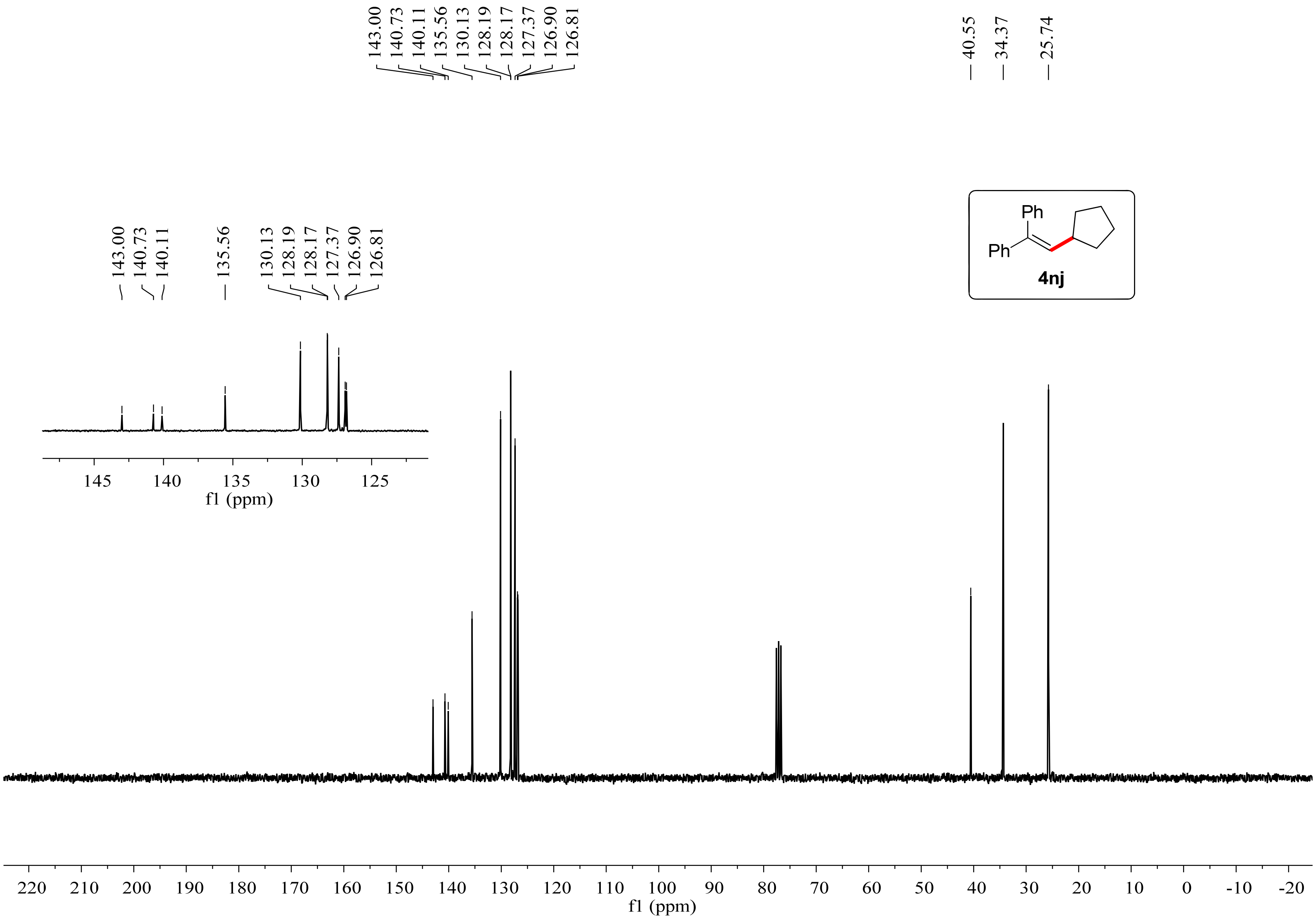
0.0
-0.5

143.00
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40.55
34.37
25.74
Ph
Ph
4nj
145
140
135
130
125
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
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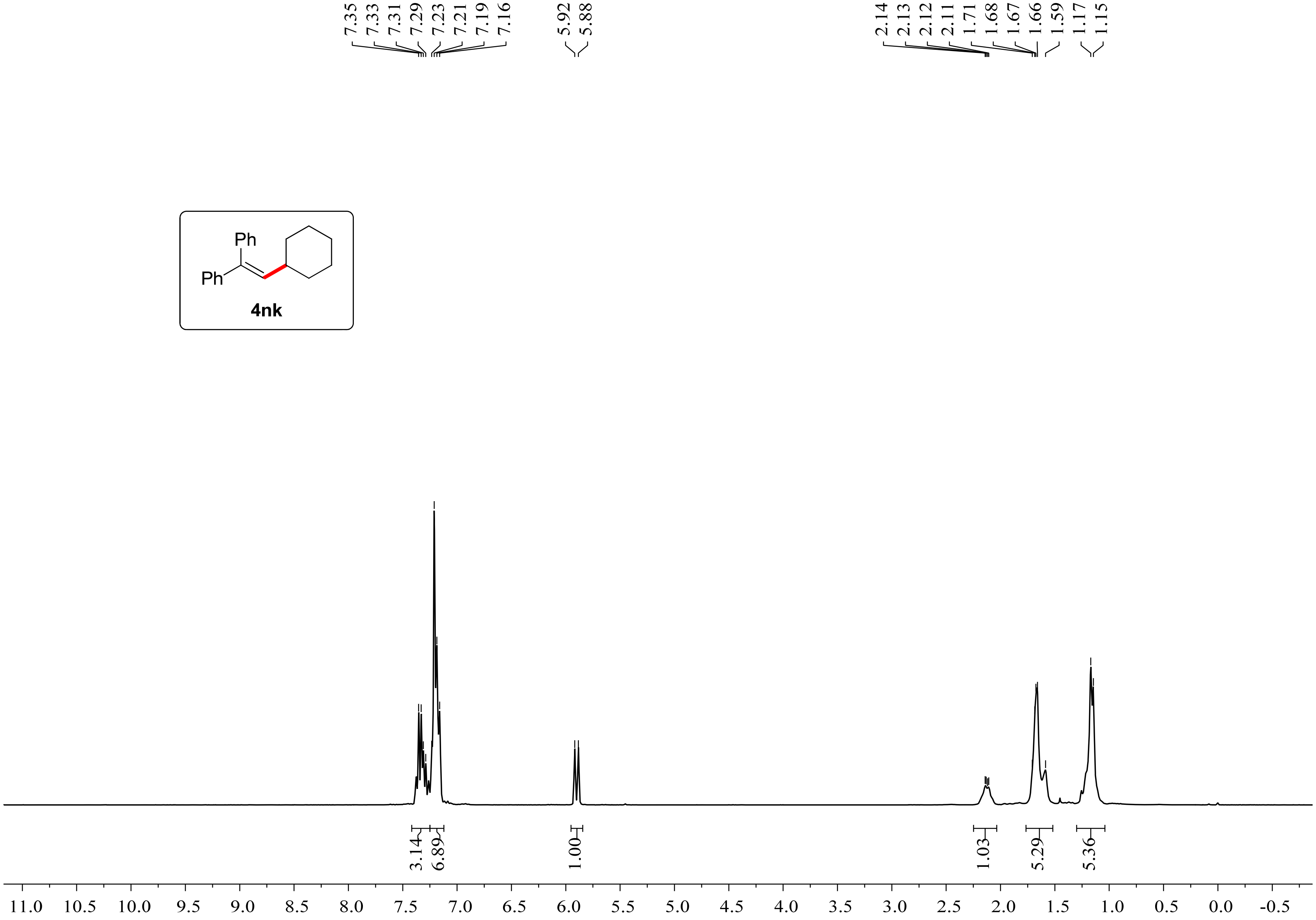
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)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2.11
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1.68
1.67
1.66
1.59
1.17
1.15
Ph
Ph
3.14
6.89
1.00
1.03
5.29
5.36
11.0
10.5
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9.0
8.5
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7.0
6.5
6.0
5.5
5.0
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2.0
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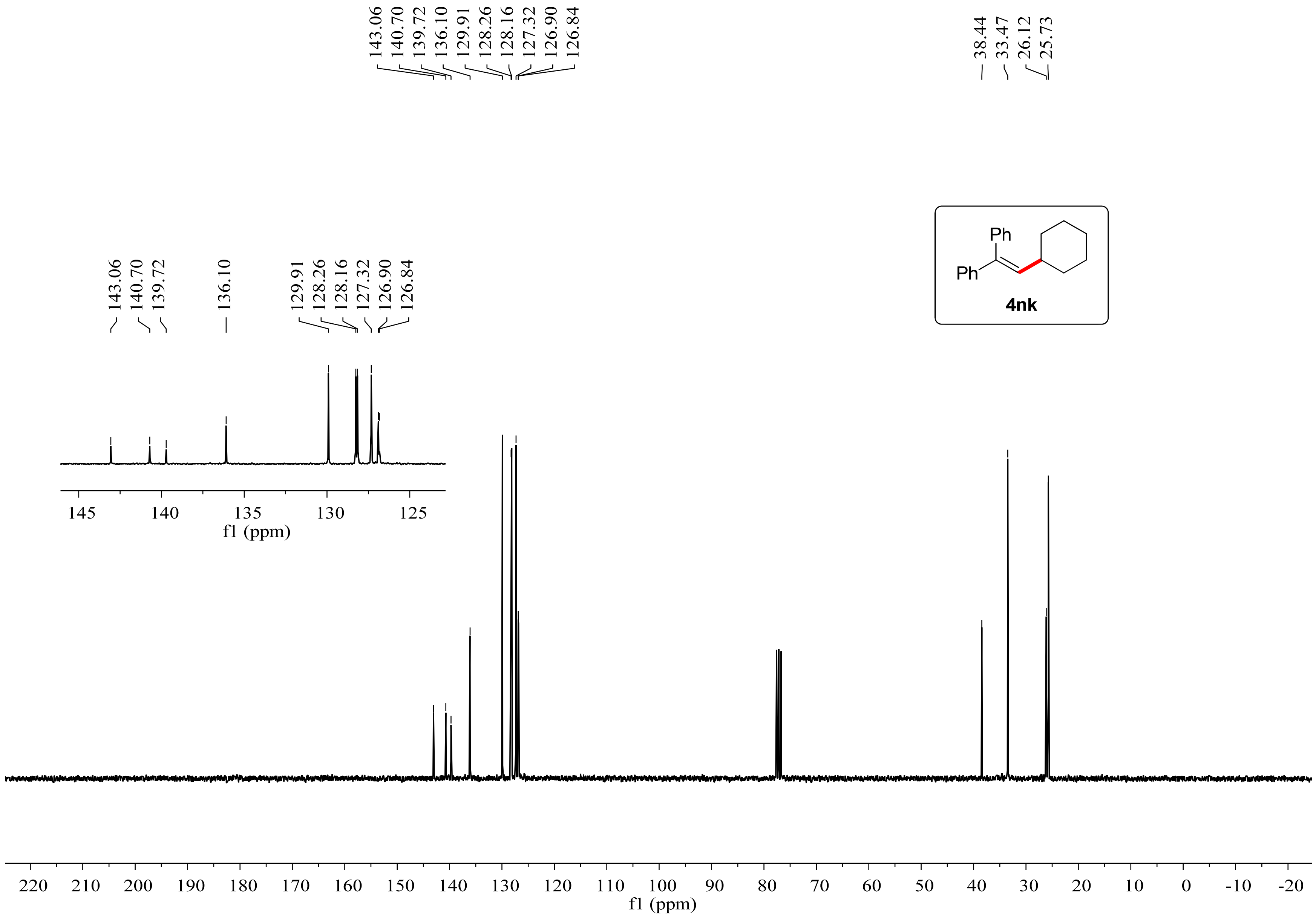
0.5
0.0
-0.5

**4nk**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38.44
33.47
26.12
25.73
145
140
135
130
125
f1 (ppm)
Ph
Ph
220
210
200
190
180
170
160
150
140
130
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80
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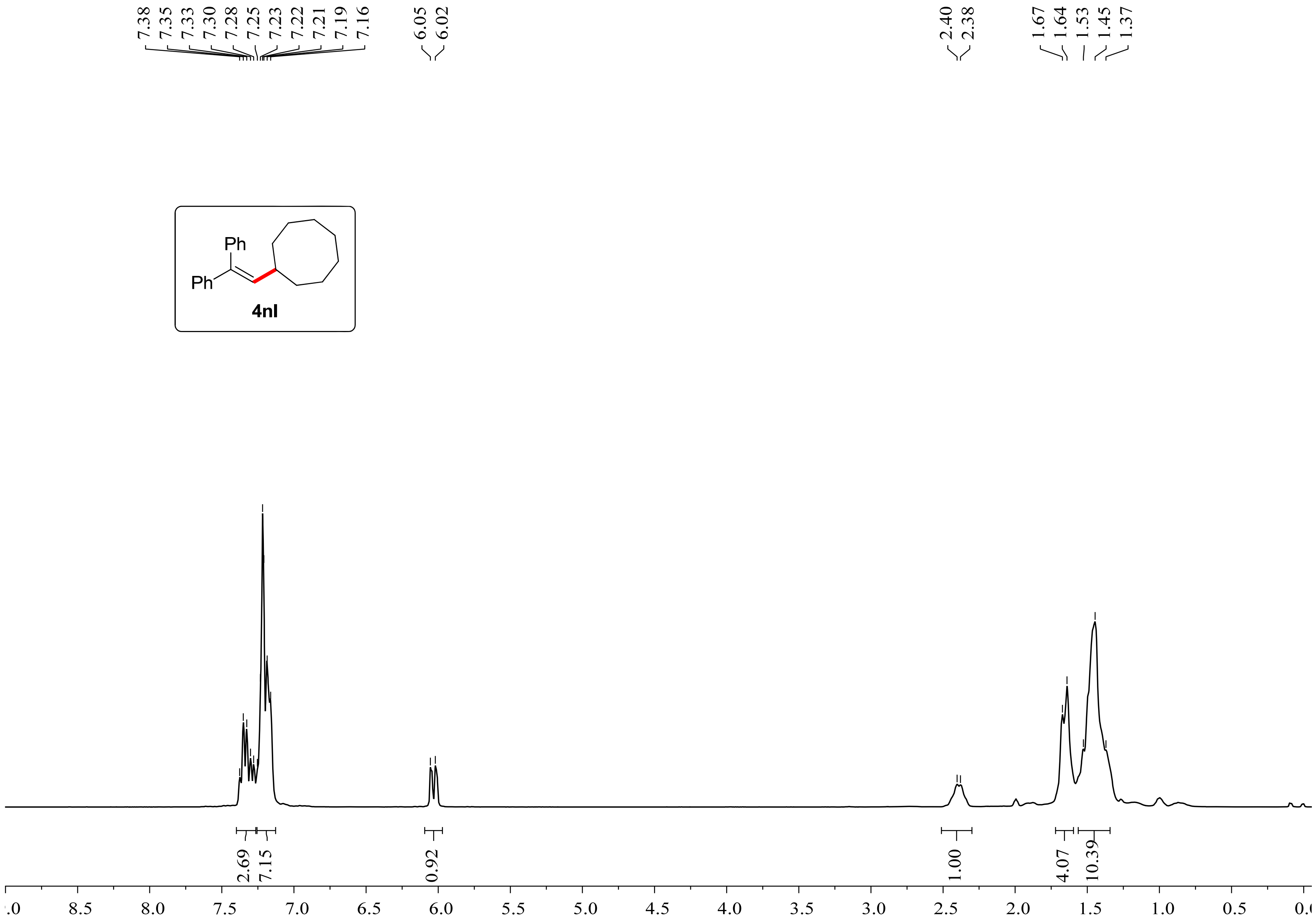
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

**4nk**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6.05
6.02
2.40
2.38
1.67
1.64
1.53
1.45
1.37
Ph
Ph
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2.69
7.15
0.92
1.00
4.07
10.39
8.5
8.0
7.5
7.0
6.5
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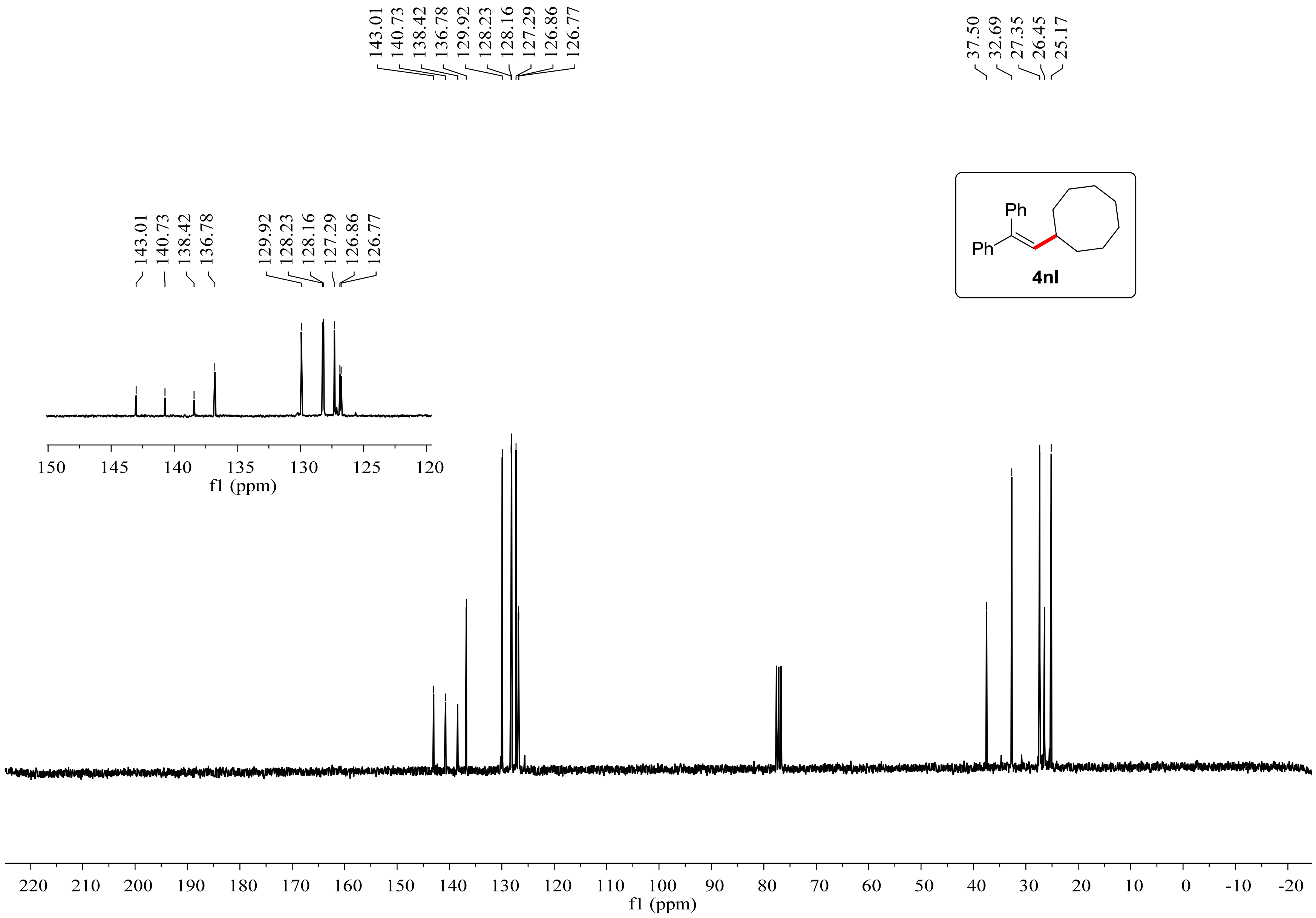
0.5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128.23
128.16
127.29
126.86
126.77
37.50
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27.35
26.45
25.17
Ph
Ph
4nl
143.01
140.73
138.42
136.78
129.92
128.23
128.16
127.29
126.86
126.77
150
145
140
135
130
125
120
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
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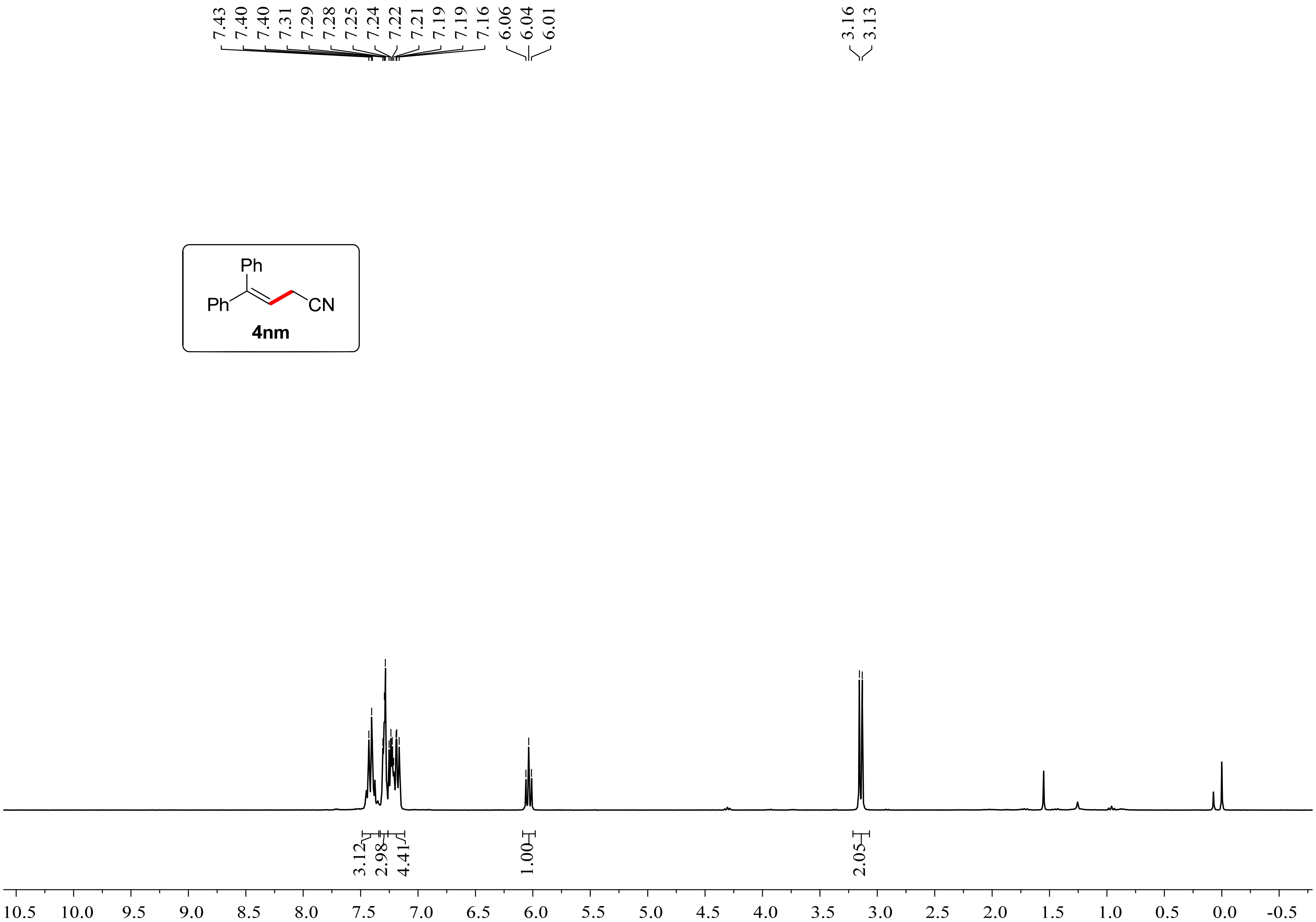
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)



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7.16
6.06
6.04
6.01
3.16
3.13
Ph
Ph
CN
4nm
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2.98
4.41
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9.0
8.5
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7.5
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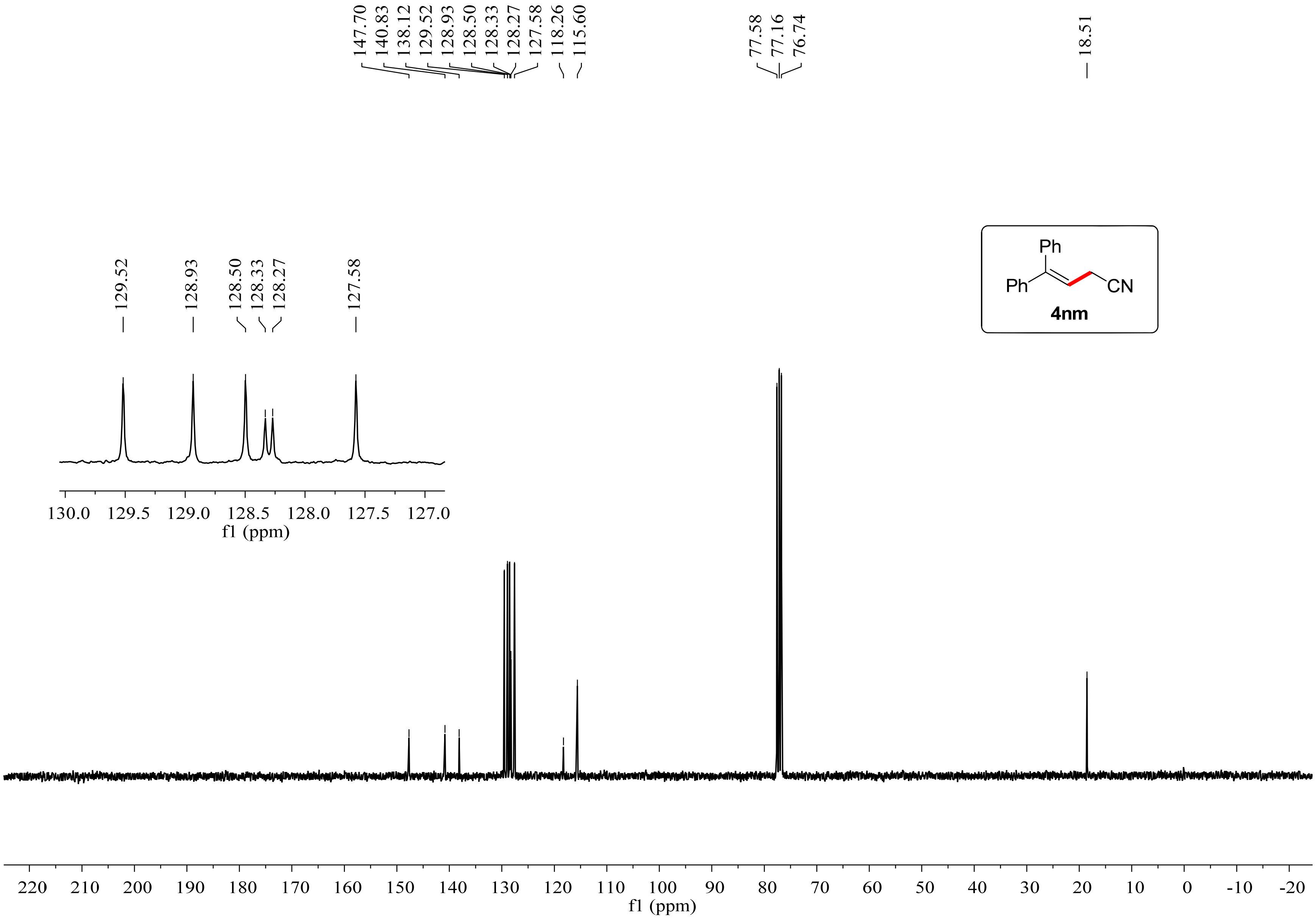
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5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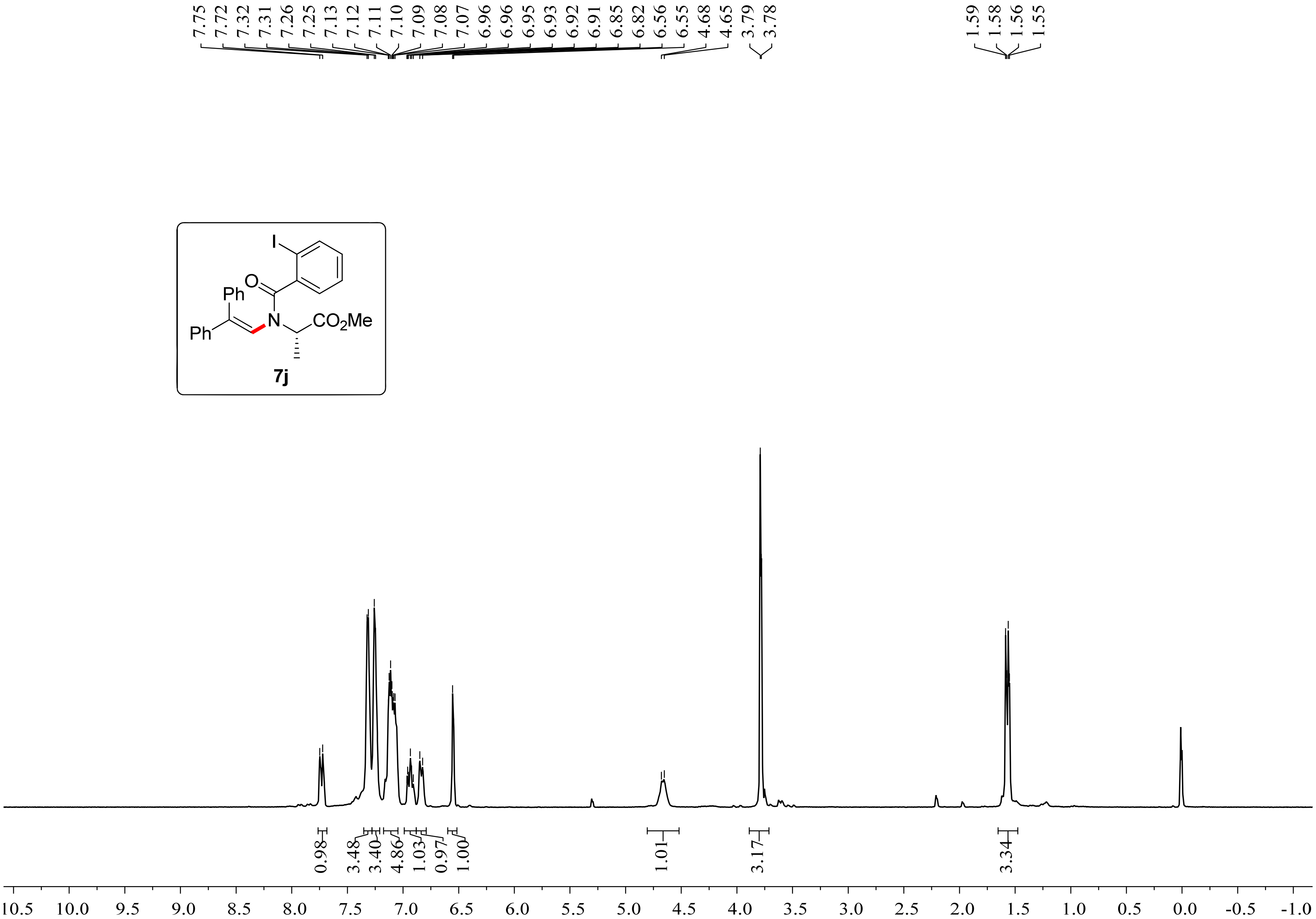
138.12
129.52
128.93
128.50
128.33
128.27
127.58
118.26
115.60
77.58
77.16
76.74
18.51
129.52
128.93
128.50
128.33
128.27
127.58
130.0
129.5
129.0
128.5
128.0
127.5
127.0
f1 (ppm)
Ph
Ph
CN
4nm
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)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7.32
7.31
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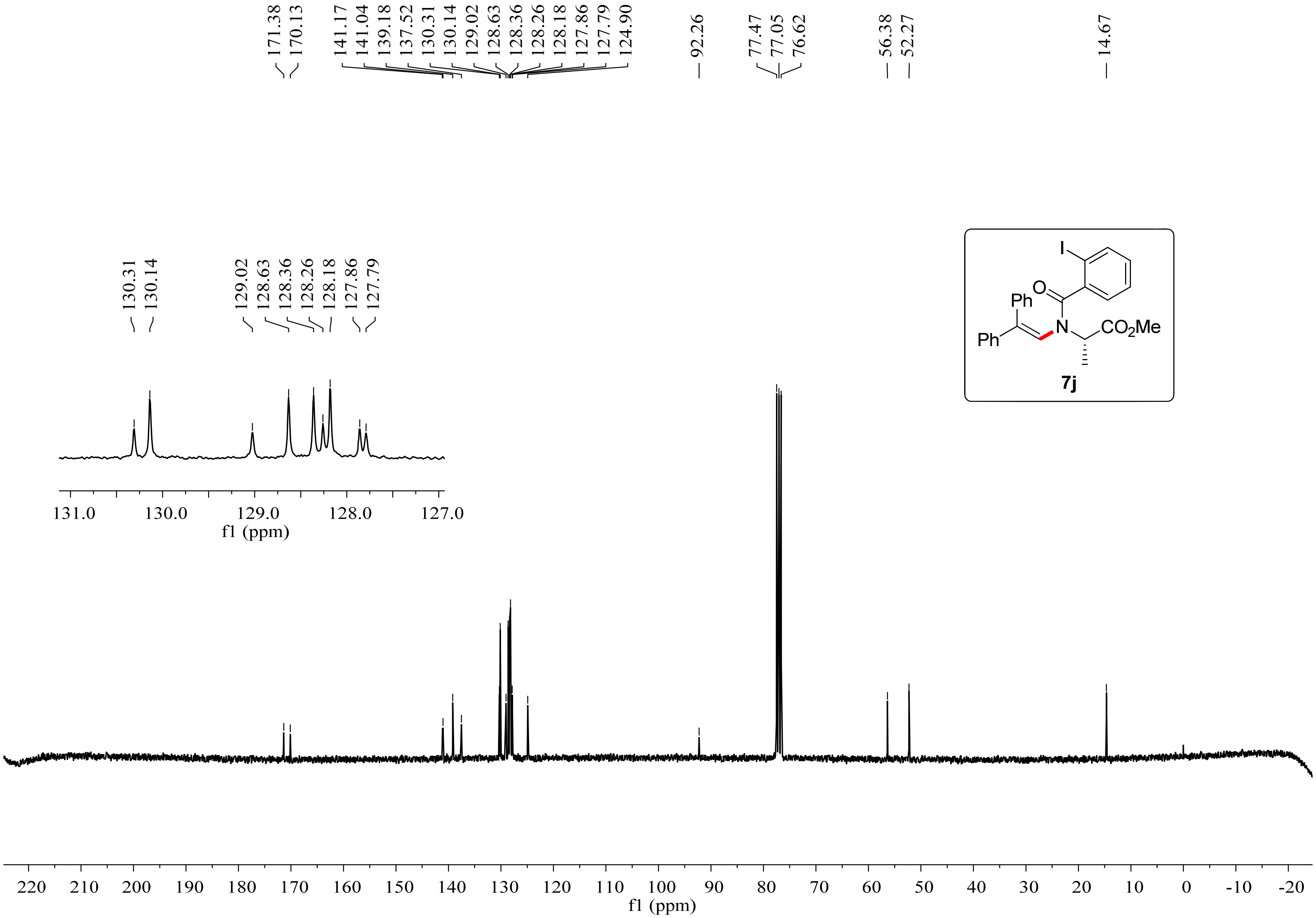
7.25
7.13
7.12
7.11
7.10
7.09
7.08
7.07
6.96
6.96
6.95
6.93
6.92
6.91
6.85
6.82
6.56
6.55
4.68
4.65
3.79
3.78
1.59
1.58
1.56
1.55
I
O
Ph
Ph
N
CO2Me
7j
0.98
3.48
3.40
4.86
1.03
0.97
1.00
1.01
3.17
3.34
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0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170.13
141.17
141.04
139.18
137.52
130.31
130.14
129.02
128.63
128.36
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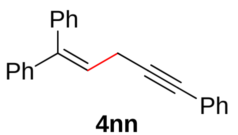
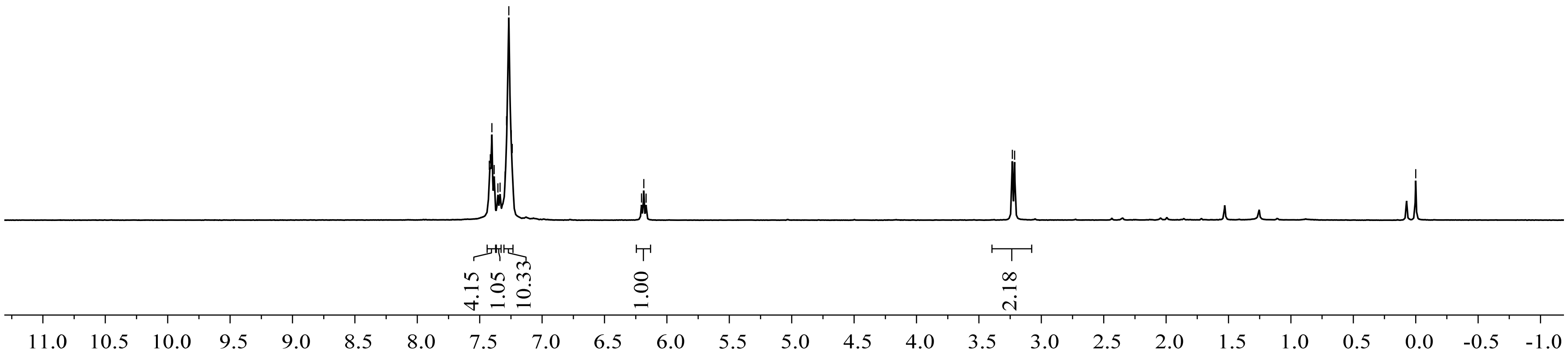
128.18
127.86
127.79
124.90
92.26
77.47
77.05
76.62
56.38
52.27
14.67
130.31
130.14
129.02
128.63
128.36
128.26
128.18
127.86
127.79
131.0
130.0
129.0
128.0
127.0
f1 (ppm)
I
O
Ph
Ph
N
CO2Me
7j
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


Ph
Ph
Ph

**4nn**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7.42
7.40
7.38
7.35
7.34
7.30
7.29
7.28
7.27
7.26
7.25
7.24
6.20
6.19
6.17
3.23
3.21
0.00
4.15
1.05
10.33
1.00
2.18
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.5
3.0
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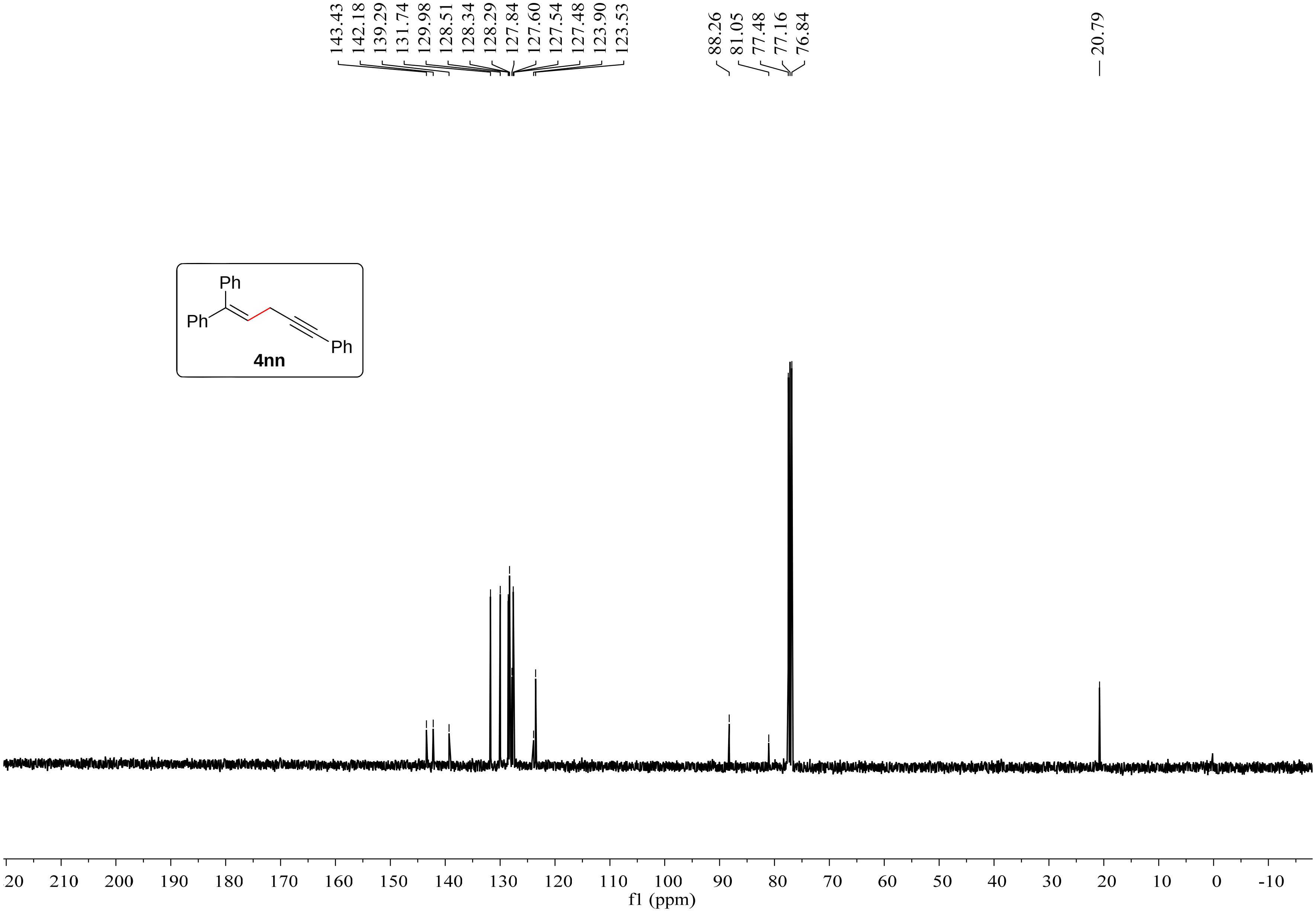
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0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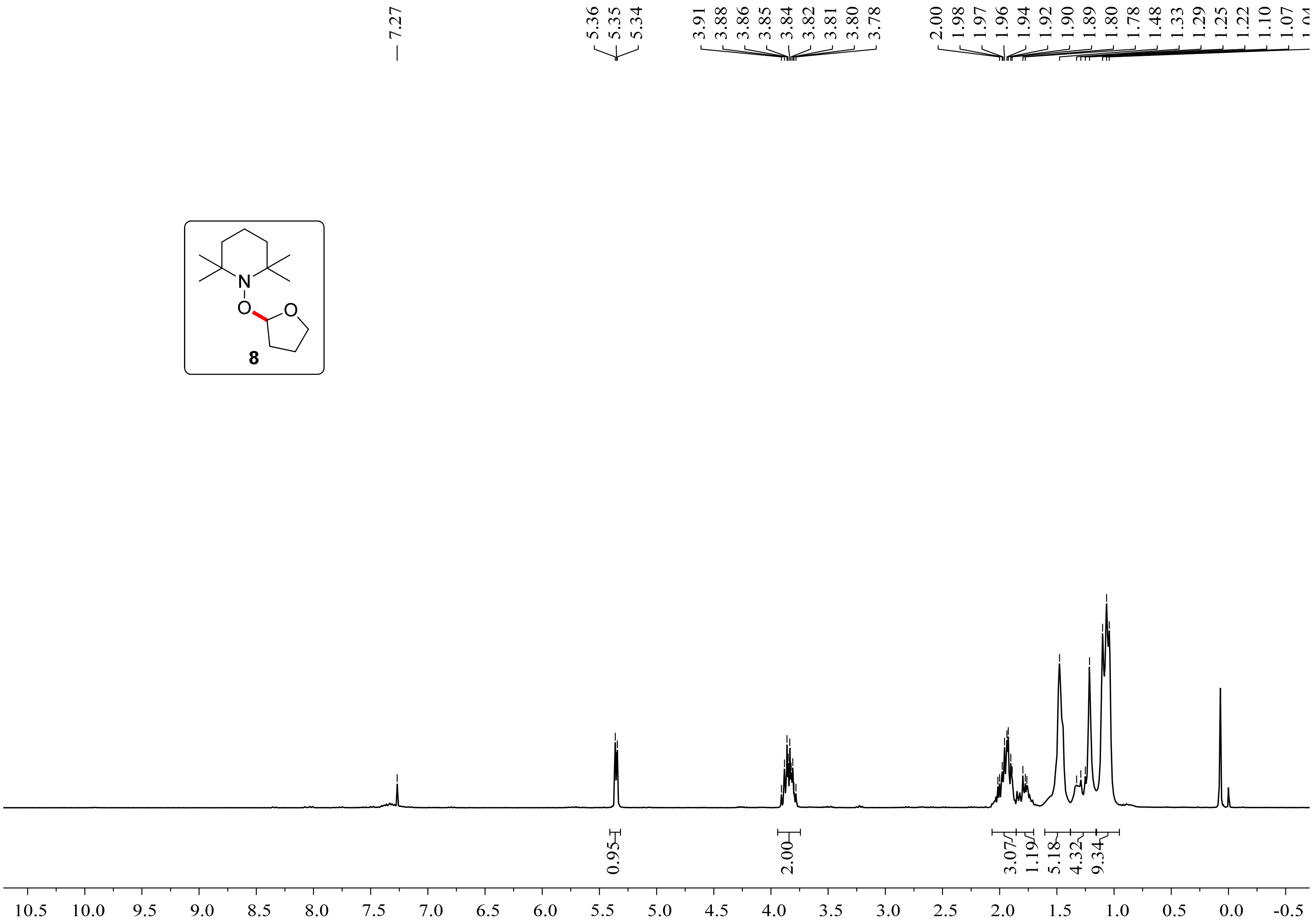
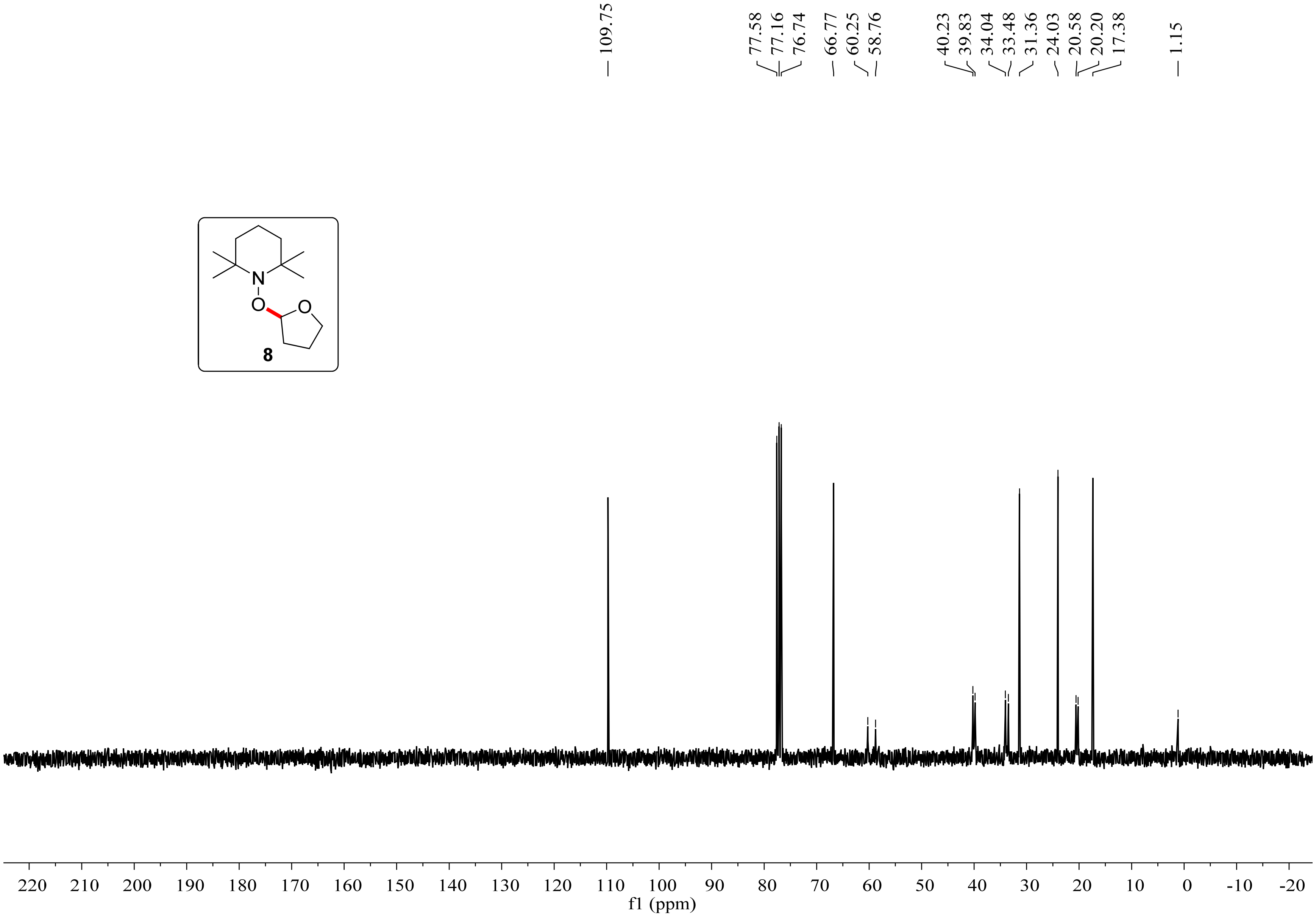
142.18
139.29
131.74
129.98
128.51
128.34
128.29
127.84
127.60
127.54
127.48
123.90
123.53
88.26
81.05
77.48
77.16
76.84
20.79
Ph
Ph
Ph
4nn
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



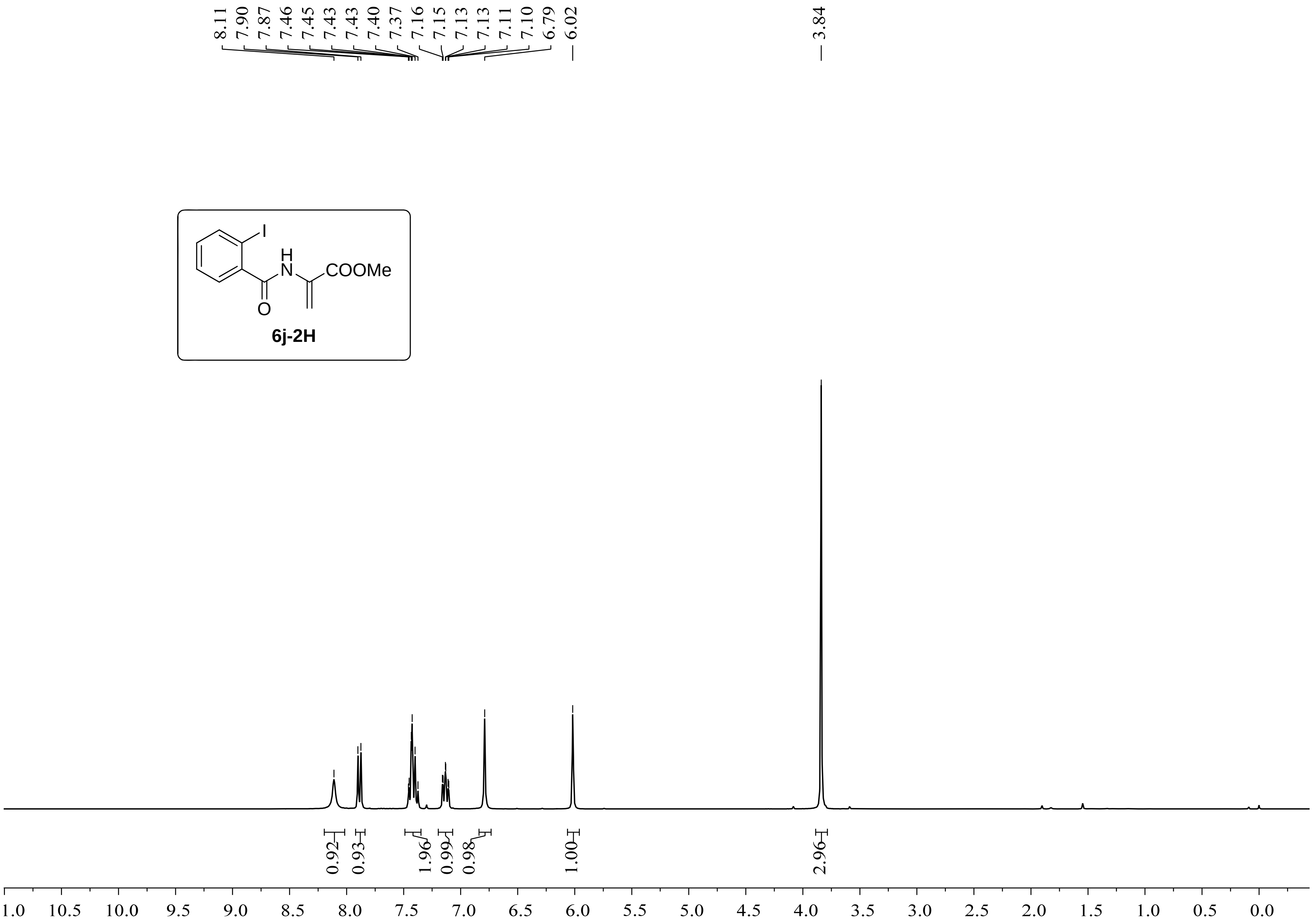
**8**

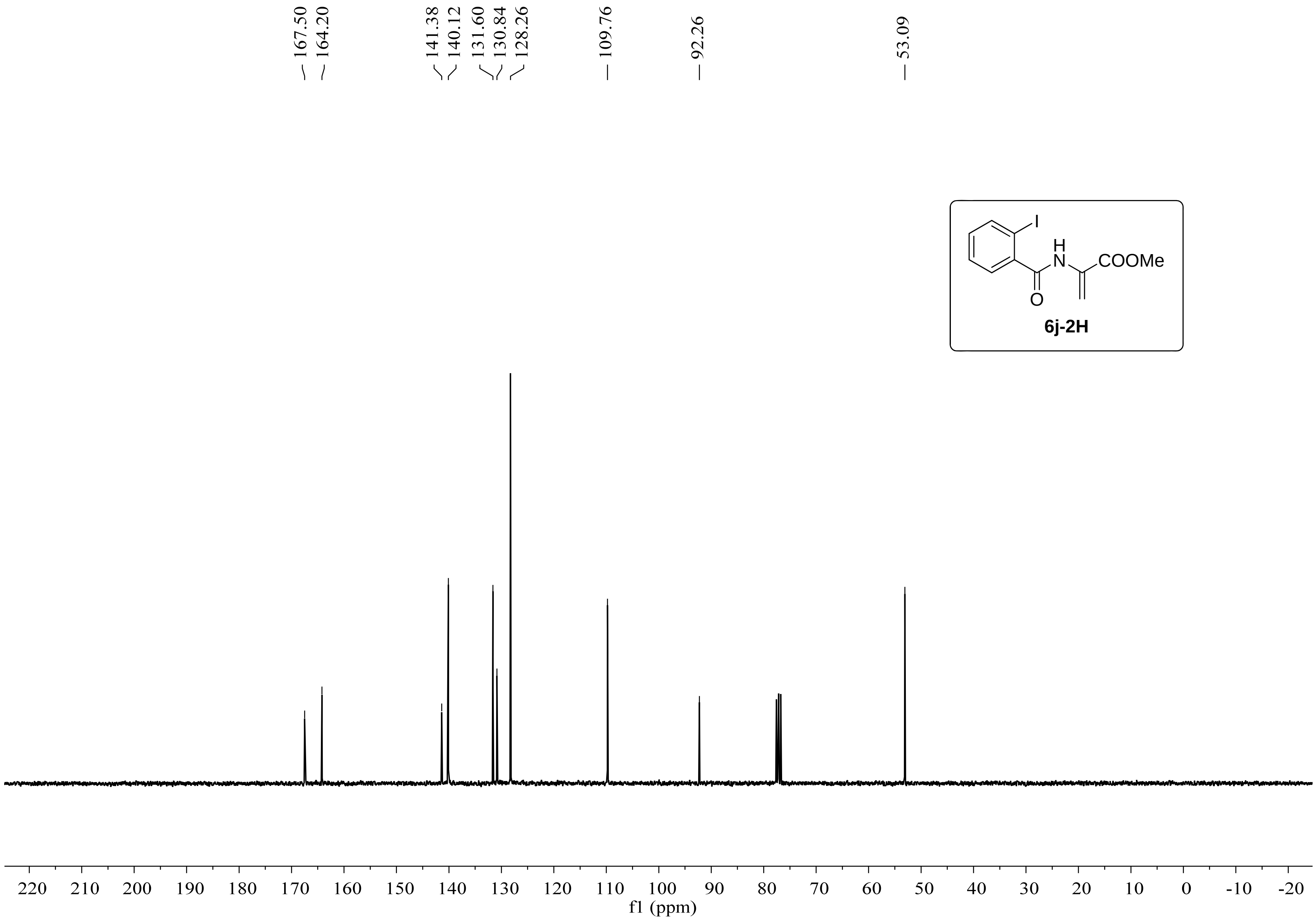
7.27
5.36
5.35
5.34
3.91
3.88
3.86
3.85
3.84
3.82
3.81
3.80
3.78
2.00
1.98
1.97
1.96
1.94
1.92
1.90
1.89
1.80
1.78
1.48
1.33
1.29
1.25
1.22
1.10
1.07
0.95
2.00
3.07
1.19
5.18
4.32
9.34
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5



**8**

109.75
77.58
77.16
76.74
66.77
60.25
58.76
40.23
39.83
34.04
33.48
31.36
24.03
20.58
20.20
17.38
1.15
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)


8.11
7.90
7.87
7.46
7.45
7.43
7.43
7.40
7.37
7.16
7.15
7.13
7.13
7.11
7.10
6.79
6.02
3.84
I
H
N
COOMe
O
6j-2H
0.92
0.93
1.96
0.99
0.98
1.00
2.96
1.0
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


167.50
164.20
141.38
140.12
131.60
130.84
128.26
109.76
92.26
53.09
I
H
N
COOMe
O
6j-2H
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)