**Supporting Information**

# Visible-Light-Promoted Oxidative Halogenation of Alkynes

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# I. General Information

## NMR Spectrum:

$^{1}H$ and $^{13}C$ spectra were collected on 400 MHz or 500 MHz NMR spectrometers (Bruker AVANCE). Chemical shifts for protons are reported in parts per million (ppm) downfield and are referenced to residual protium in the NMR solvent ($CHCl_3$ = δ 7.26). Chemical for carbon are reported in parts per million downfield and are referenced to coupling of carbon nucleus on deuterium ($CHCl_3$ = δ 77.0). Date are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = double, t = triplet, q = quartet, m = multiplet ), coupling constants in Hertz (Hz), integration.

## Mass Spectroscopy:

Mass spectra were in general recorded on a Waters Synapt G2 (HRMS) and Waters Acquity H (LCMS).

## Chromatography:

Column chromatography was performed with silica gel (300 – 400 mesh ASTM).

## IR:

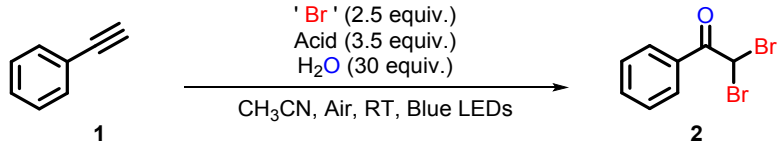
SHIMADZU IR Tracer-100 Spectrometers. TENSOR (27) Series FT-IR Spectrometers.

## Solvent:

$CH_3CN$ was dried with $CaH_2$ and distilled using standard methods. Distilled water was bought and used without further purification.

# II. Conditions Optimization

**Table S1:** Condition optimization of oxybromonation.[a]

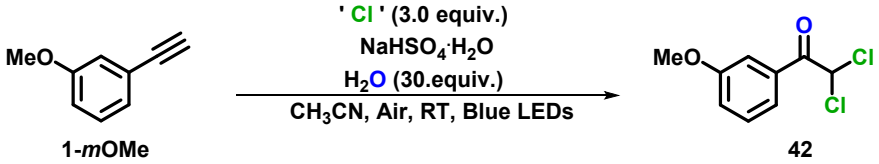



**1** **2**

| Entry | ' Br ' Source | Acid | Yield (%)[b] |
|---|---|---|---|
| 1 | NaBr | $CH_3COOH$ | 7 |
| 2 | NaBr | CSA | 69 |
| 3 | NaBr | $H_3PO_4$ | 57 |
| **4** | **NaBr** | **$NaHSO_4{\cdot}H_2O$** | **89(85)[c]** |
| 5 | KBr | $NaHSO_4{\cdot}H_2O$ | 69 |
| 6 | LiBr | $NaHSO_4{\cdot}H_2O$ | 82 |
| 7 | $NH_4Br$ | $NaHSO_4{\cdot}H_2O$ | 77 |
| 8 | $MgBr_2$ | $NaHSO_4{\cdot}H_2O$ | 64 |

[a]The reaction conditions: **1** (0.2 mmol), $H_2O$ (6.0 mmol), Acid (0.7 mmol), "Br" (0.5 mmol), MeCN (2.0 mL), room temperature, air, 6 W blue LEDs, 8 h. [b] NMR yield with $CH_2Br_2$ as internal standard. [c] isolated yield.

**Table S2:** Condition optimization of oxychloronation.[a]

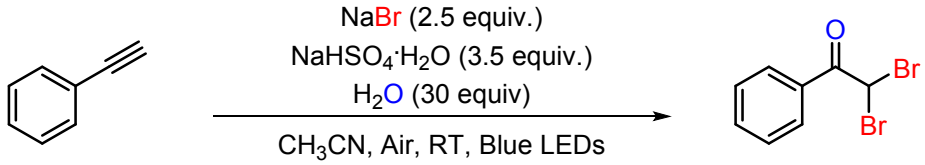



**1-*m*OMe** **42**

| Entry | ' Cl ' Source | Acid (3.5 equiv.) | Yield (%)[b] |
|---|---|---|---|
| 1 | NaCl | $NaHSO_4{\cdot}H_2O$ | 59[b] |
| 2 | LiCl | $NaHSO_4{\cdot}H_2O$ | 70 |
| 3 | KCl | $NaHSO_4{\cdot}H_2O$ | 63 |
| 4 | $MgCl_2$ | $NaHSO_4{\cdot}H_2O$ | 41 |
| 5 | $NH_4Cl$ | $NaHSO_4{\cdot}H_2O$ | 65 |
| **6** | **LiCl** | **$NaHSO_4{\cdot}H_2O$ (4.0 equiv.)** | **75 (71)[c]** |
| 7 | LiCl | $KHSO_4$ | 60 |

[a]The reaction conditions: **1-*m*OMe** (0.2 mmol), $H_2O$ (6.0 mmol), $NaHSO_4{\cdot}H_2O$ (0.8 mmol), "Cl" (0.6 mmol), MeCN (2.0 mL), room temperature, air, 6 W blue LEDs, 24 h. [b] NMR yield with $CH_2Br_2$ as internal standard. [c] isolated yield.

**Table S3:** Variation from standard conditions




**1** **2**

| Entry | Variation from standard conditions | Yield (%)[a] |
|---|---|---|
| 1 | none | 89 |
| 2 | none[b] | 77 |
| 3 | $N_2$ instead of air | NR |
| 4 | $O_2$ instead of air | 48 |
| 5 | no light | NR |
| 6 | no light, 70 $^oC$ | NR |
| 7 | no NaBr | ND |
| 8 | no $NaHSO_4{\cdot}H_2O$ | Trace |
| 9 | no $H_2O$ | 70 |
| 10 | only NaBr | Trace |
| 11 | only $NaHSO_4{\cdot}H_2O$ | NR |
| 12 | only $H_2O$ | NR |

[a]NMR yield with $CH_2Br_2$ as internal standard. [b]the schlenk tube (25 mL) were sealed.

# III. Mechanistic Studies

## 1) Ultraviolet–visible Absorption Experiments

Ultraviolet–visible absorption experiments were performed using a Shimadzu UV-2700 UV-visible spectrophotometer. In each experiment, the varying samples were combined in $CH_3CN$ in screw-top 1.0 cm quartz cuvettes.

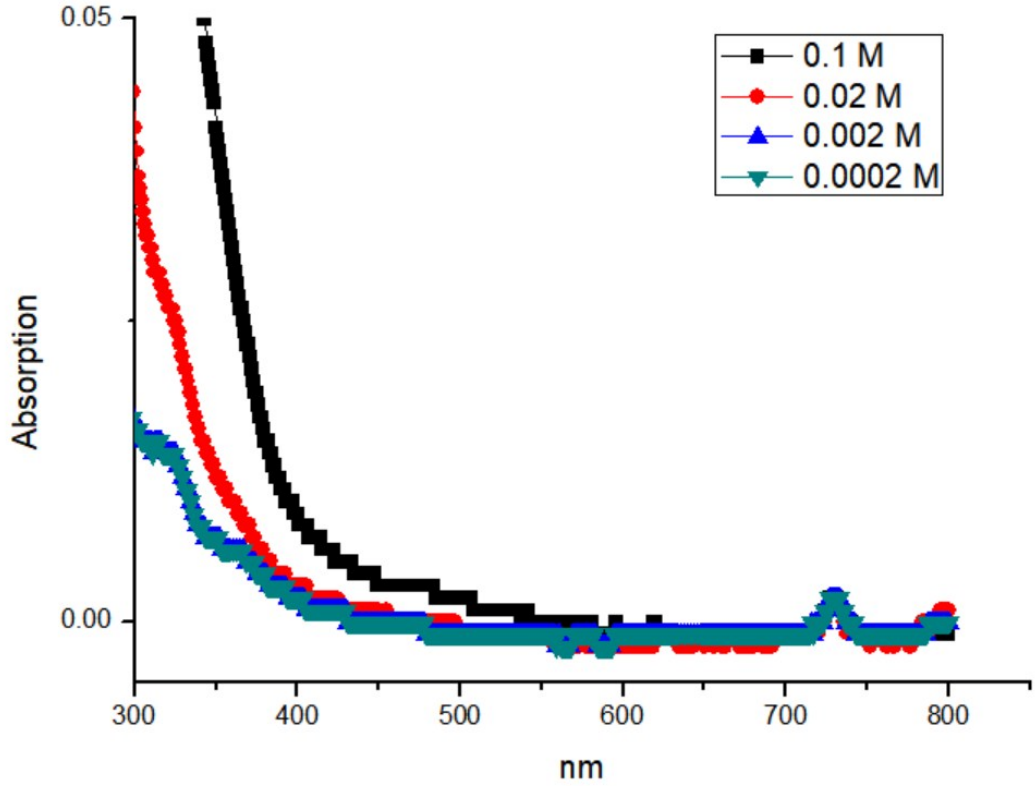



**Figure S1:** Ultraviolet–visible absorption of **1**.

## 2) Stern–Volmer Fluorescent Quenching Experiments

Fluorescence quenching studies were performed using a Shimadzu RF-6000 Fluorescence Spectrophotometer. In each experiment, the photocatalyst and varying concentrations of quencher were combined in $CH_3CN$ in screw-top 1.0 cm quartz cuvettes. For the emission quenching of phenylacetylene (0.1 M), the solution was irradiated at 299 nm, and the emission intensity was observed at 347 nm.

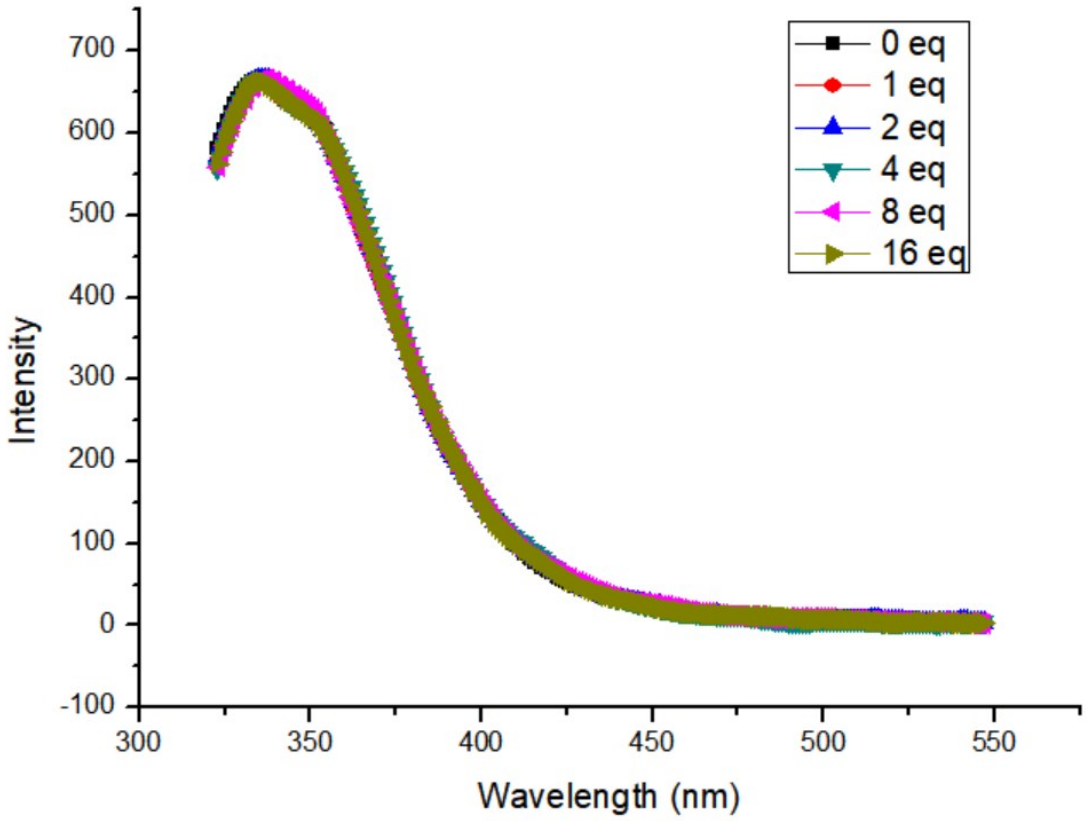



**Figure S2:** Quenching experiments of **1** with sat. $NaHSO_4 \cdot H_2O$ (aq).

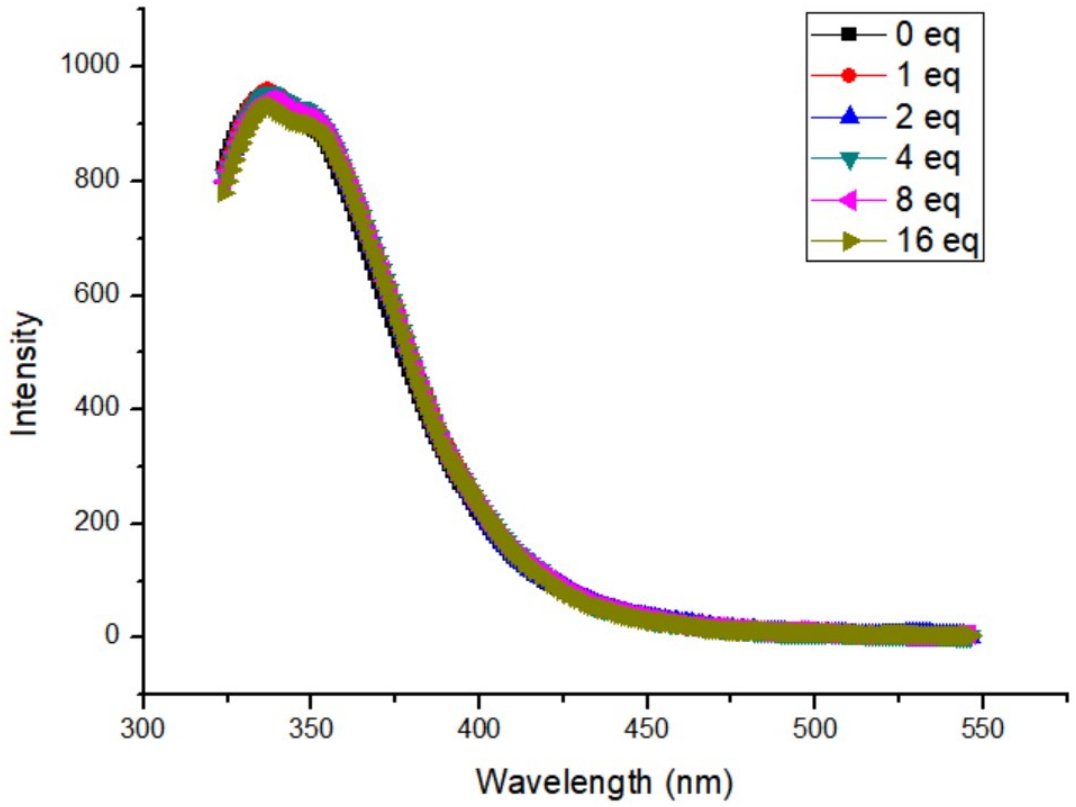



**Figure S3:** Quenching experiments of **1** with sat. NaBr (aq).

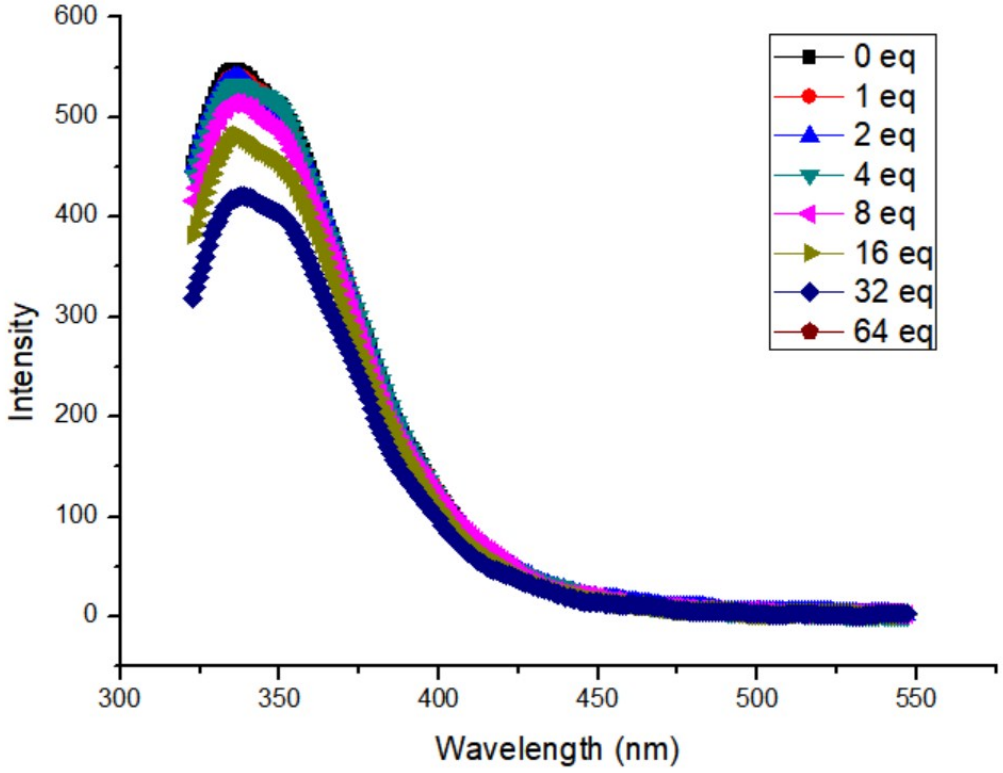



**Figure S4:** Quenching experiments of **1** with HBr (aq).

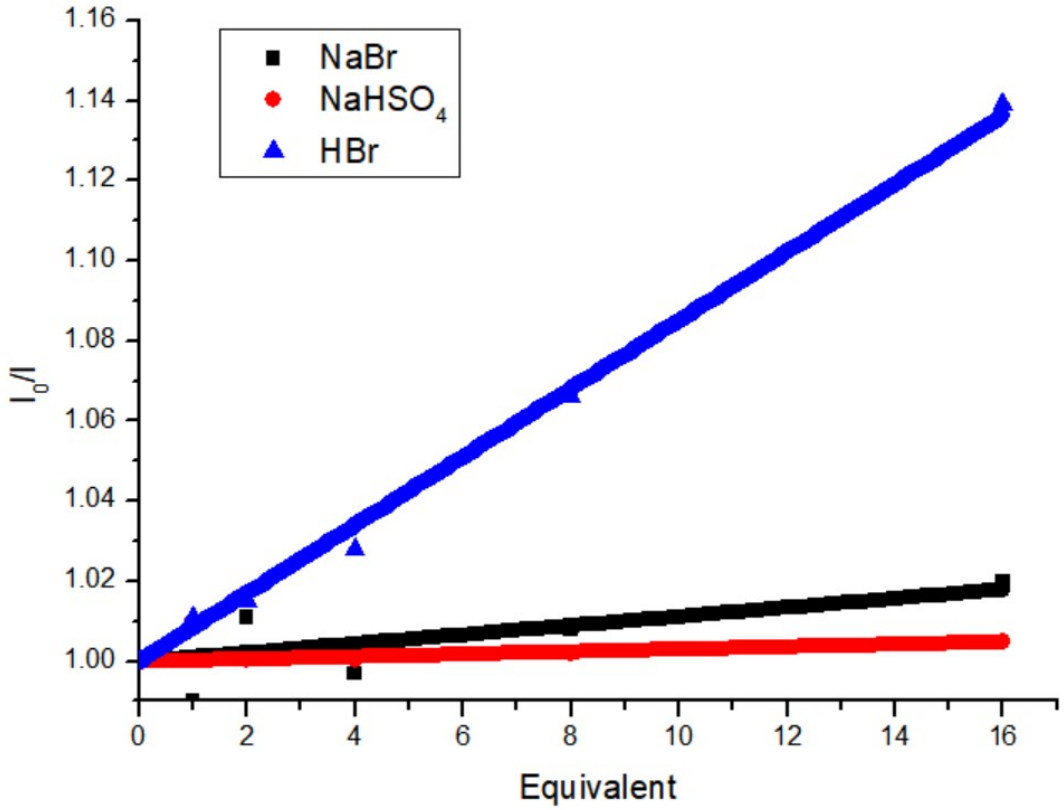
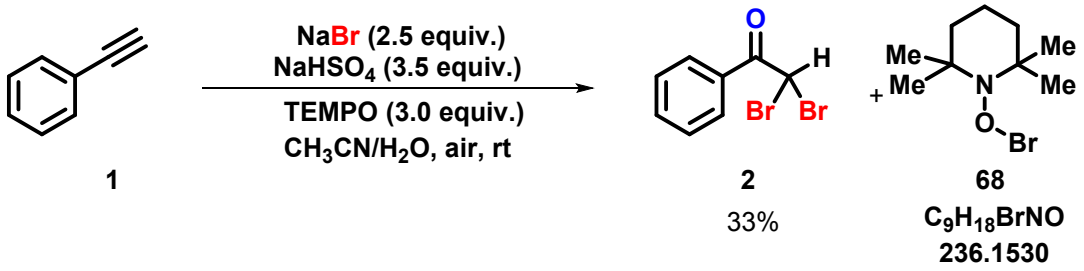


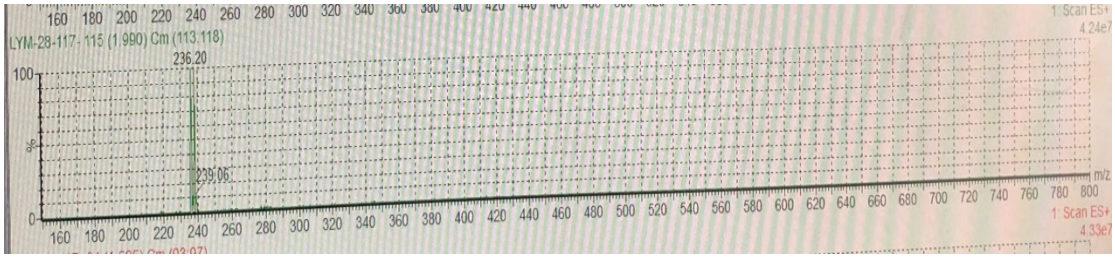

**Figure S5:** Fluorescent quenching experiments of **1** with different reagents.

### 3) Radical Trapping Experiments with TEMPO

All reactions were operated under standard conditions with extra TEMPO (2 equiv.). The yields of **2** were determined with NMR.




**1** **2** 33% **68** $C_9H_{18}BrNO$ 236.1530



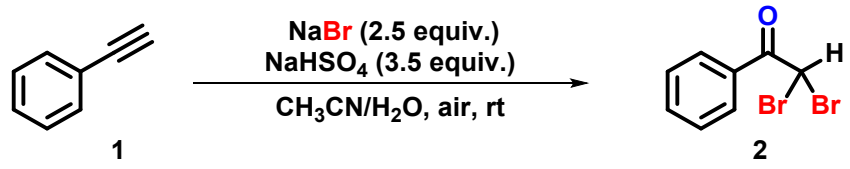

### 4) Radical Clock Experiment


**69** **70** 30%

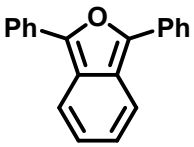
## 5) Control Experiments

All the reactions were conducted under standard conditions with certain amount of additives. The corresponding yields were calculated by NMR with $CH_2Br_2$ as internal standard.

**Table S3:** Control Experiments.




1 2

| Entries | Additives | Fucntion | Results |
|---|---|---|---|
| 1 | $NaN_3$ (1 equiv.) | $^1O_2$ inhibitor | 87% |
| 2 |  (1 equiv.) | $^1O_2$ inhibitor<br>$O_2^{\cdot-}$ inhibitor | 83% |
| 3 | tBuOH (1 equiv.) | $HO^{\cdot}$ inhibitor | 88% |

## 6) Electron paramagnetic resonance experiments

The electron paramagnetic resonance (EPR) experiments were recorded on an X-band Bruker E500 10/12. A reaction system with $UO_2(OAc)_2 \cdot 2H_2O$ (0.004 mmol), sulfide 1a (0.2 mmol), DMPO[a] (0.1 mmol), $CH_3CN$ (1 mL) was irradiated with blue light (2w*3) under oxygen atmosphere with paralleled reactor. After 10 mins, melting-point tube was used to suck certain amount of reaction system, then, both ends were melted by fire. This sample was submitted for the EPR experiments.

[a]DMPO = 5,5-dimethyl-1-pyrroline-1-oxide.

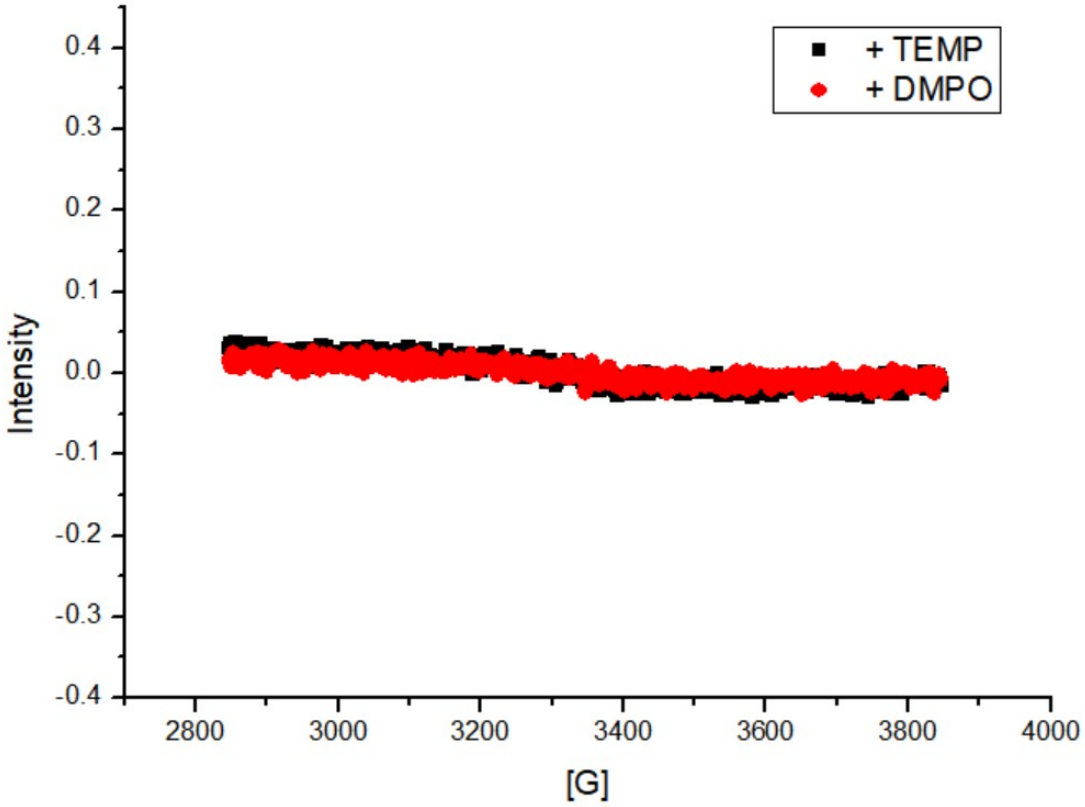



**Figure S6:** EPR spectrums.

No obvious $^1O_2$, $HO^{\bullet}$ and $O_2^{-\bullet}$ in standard system

## 7) Studies on Hydrogen Peroxide

The amount of $H_2O_2$ was determined by titration with iodide ion, as described previously in the literature in which the reflux procedures was instead by stirring at room temperature.(*1*) In an iodometric titration, the formation of $I_3^-$ and the consumption of $H_2O_2$ follows a one-to-one ratio as eqs S1-3. The concentration $H_2O_2$ can be derived from the concentration of $I_3$ (Abs@361 nm = $\varepsilon b[I_3^-]$). All iodometric titrations are conducted anaerobically to avoid the oxidation of $I^-$ to $I_3^-$ by $O_2$.[2]

$$2\,H_2O_2 + 2\,I^- \longrightarrow H_2O + 1/2\,O_2 + I_2 \quad \text{(eq S1)}$$

$$I_2 + I^- \longrightarrow I_3^- \quad \text{(eq S2)}$$

$$H_2O_2 + 2\,I^- \longrightarrow H_2O + 1/2\,O_2 + I_3^- \quad \text{(eq S3)}$$

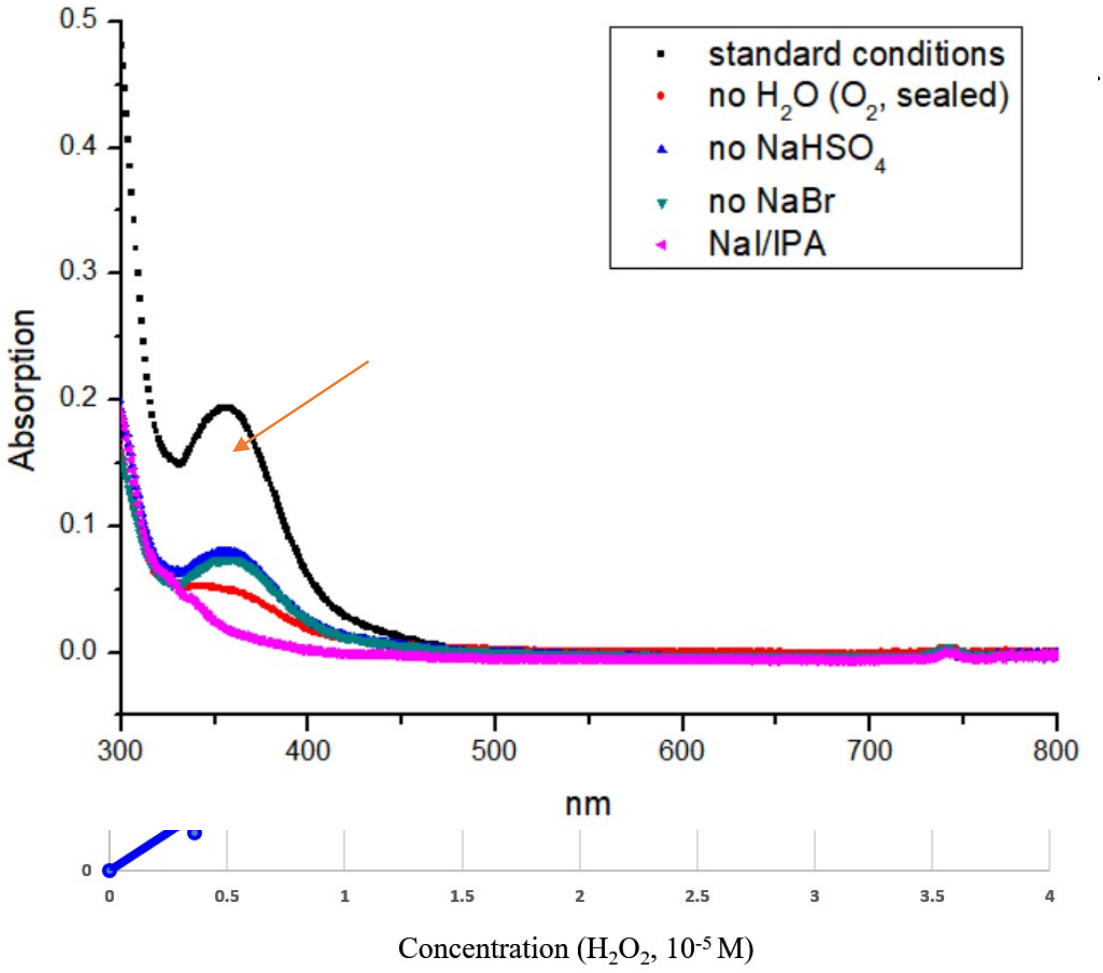
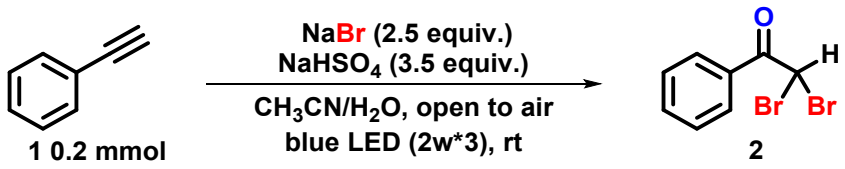



**Figure S7:** Standard curve of the amount of $I_3^-$ for its quantitative studies.

## 8) Quantitative Studies of $H_2O_2$.

**Table S4:** Control experiments based on the generation of $H_2O_2$ under standard oxybromoation conditions.




1 0.2 mmol

2

| Entries | Conditions | in-situ generated $H_2O_2$ |
|---|---|---|
| 1 | standard conditions | 0.112 mmol |
| 2 | no $H_2O$ ($O_2$, sealed) | 0.021 mmol |
| 3 | no $NaHSO_4$ | 0.040 mmol |
| 4 | no NaBr | 0.038 mmol |

## 9) Oxygen Labelling Reactions

These reactions are conducted under standard sulfoxidation or sulfonation conditions with $^{18}O_2$ instead of $O_2$.

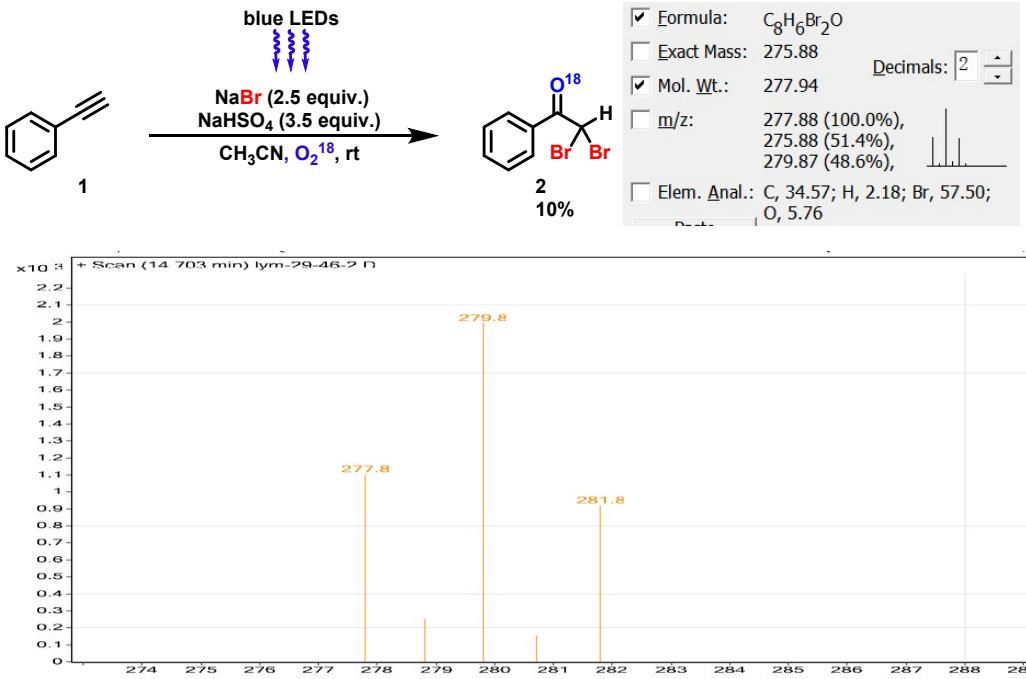



**Figure S8:** GCMS spectrum for labelling experiments with $O_2{}^{18}$.

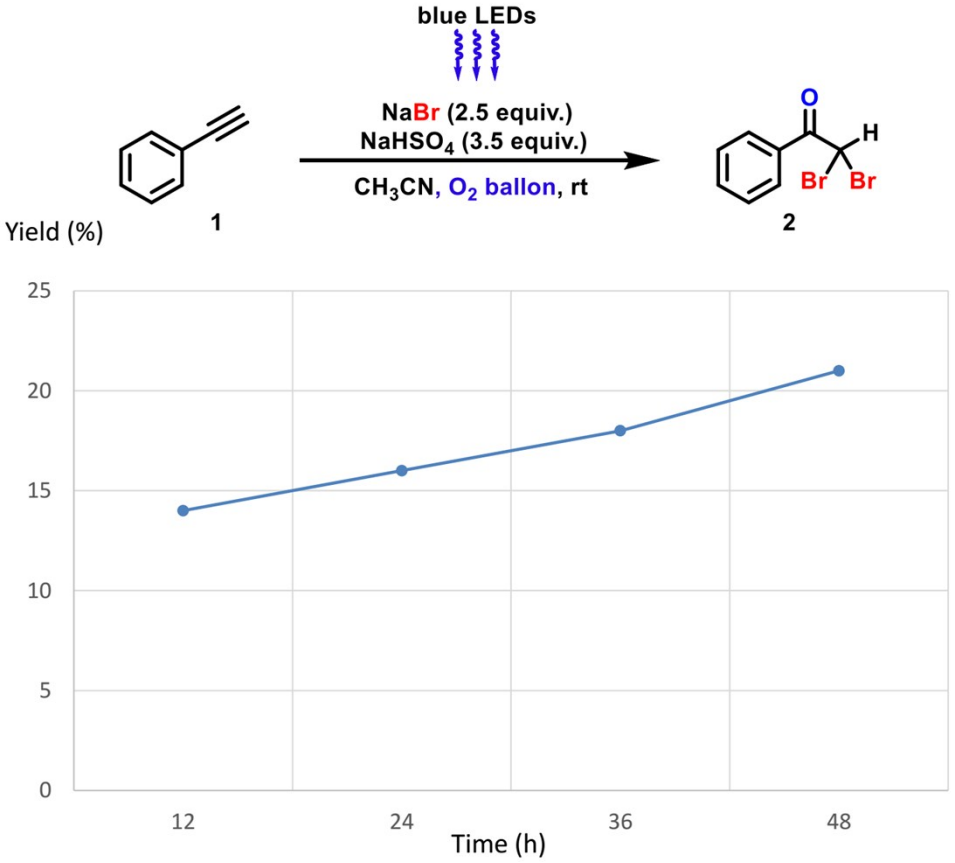
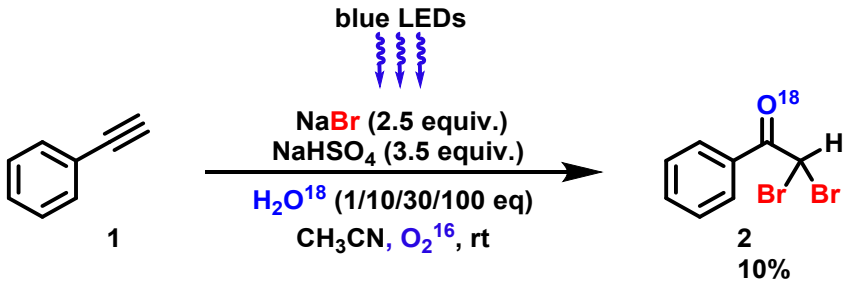
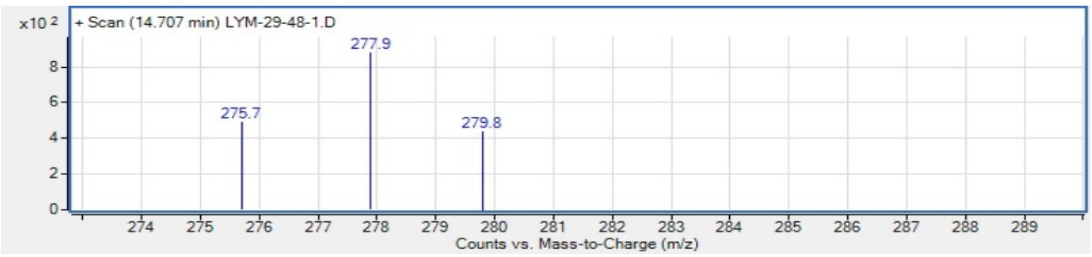



**Figure S9:** Tracking Experiments without $H_2O$

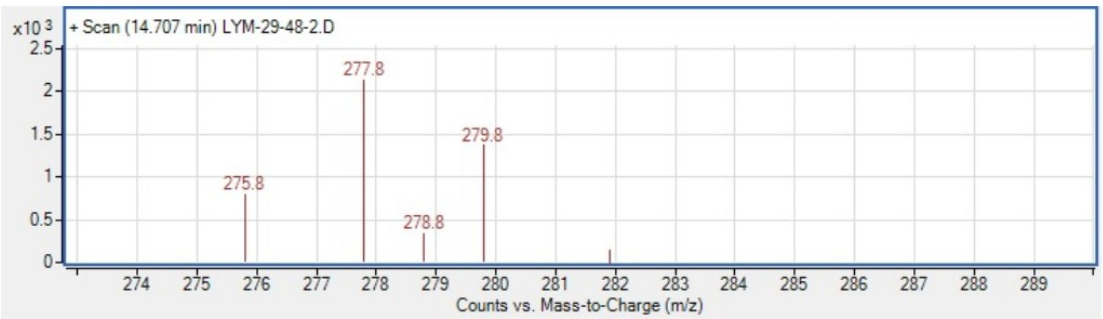
Tracking experiments indicate $H_2O$ is necessary due to the low efficiency with only $O_2$.




$H_2O^{18}$ (1 eq) 276/282 = 1/0




$H_2O^{18}$ (10 eq) 276/282 ≈ 1/0.23




$H_2O^{18}$ (30 eq) 276/282 ≈ 1/3

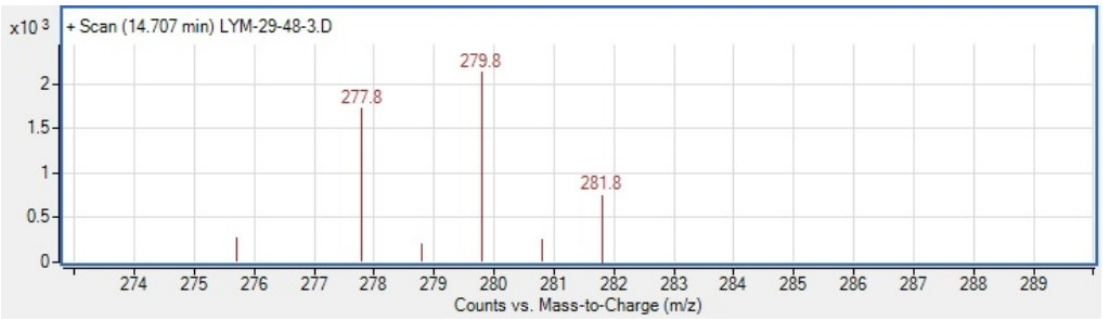
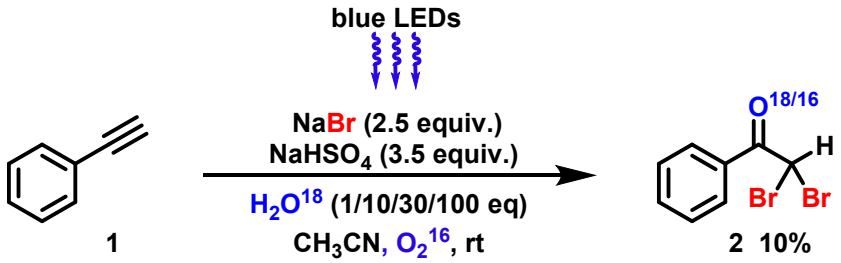


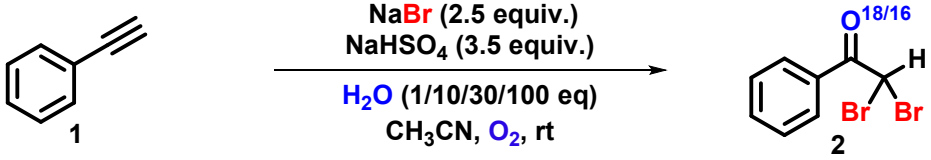

**Figure S10:** GCMS spectrum for labelling experiments with different amount of $H_2O^{18}$.

**Table S5:** Results of labelling experiments with different amount of $H_2O^{18}$.



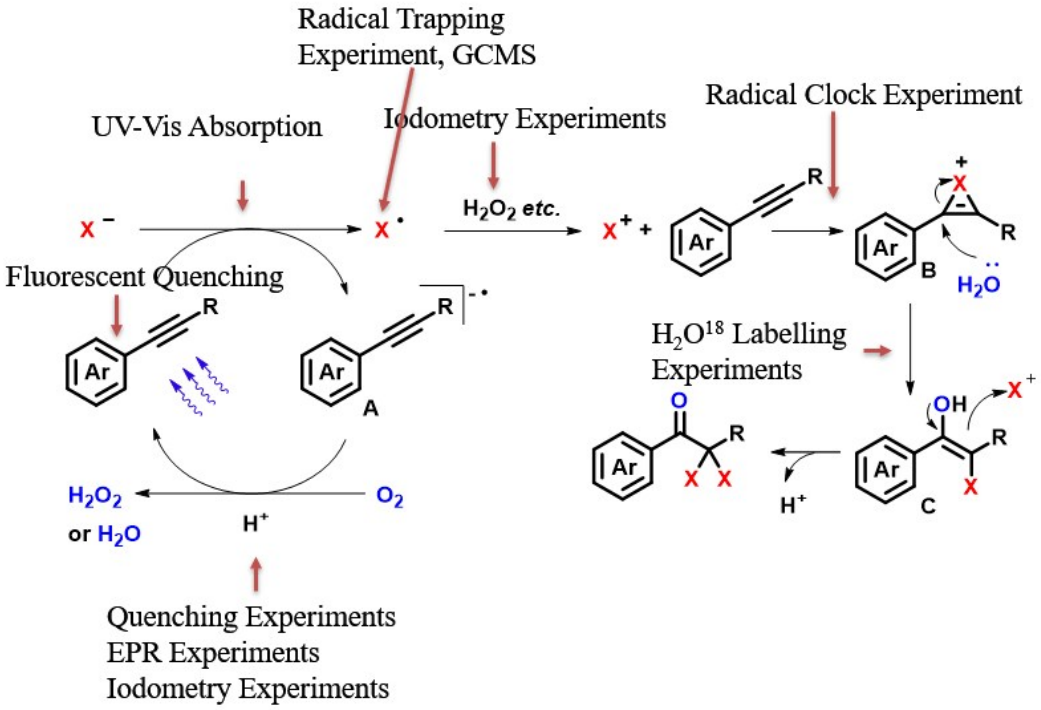

| Entries | $H_2O^{18}$ (x eq) | MS(276)/MS(282) | NMR Yield of 2 (%) |
|---|---|---|---|
| 1 | 1 | 1/0 | 32% |
| 2 | 10 | 1/0.23 | 52% |
| 3 | 30 | 1/3 | 84% |

## 10) Oxygen-Labelling Experiments




| Entries | $O_2$ | $H_2O$ | MS(276)/MS(282) | 2 (NMR Yields) |
|---|---|---|---|---|
| 1 | - | $H_2O$ (30 equiv.) | - | 0% |
| 2 | $O_2^{18}$ | - | 0/1 | 10% |
| 3 | $O_2^{16}$ | $H_2O^{18}$ (30 equiv.) | 1/3 | 84% |
| 4 | $O_2^{18}$ | $H_2O^{18}$ (30 equiv.) | 0/1 | 73% |

## 11) Proposed Mechanism

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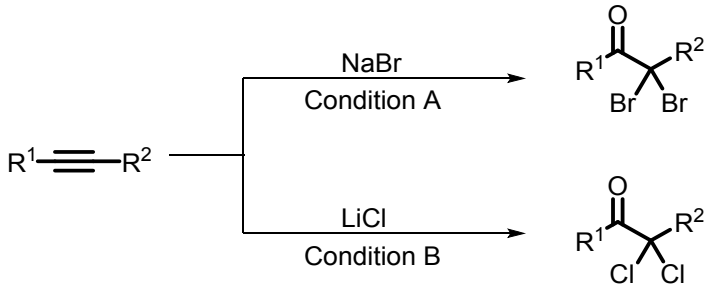
# IV. The Procedure and Data for Oxyhalogenation of Alkynes

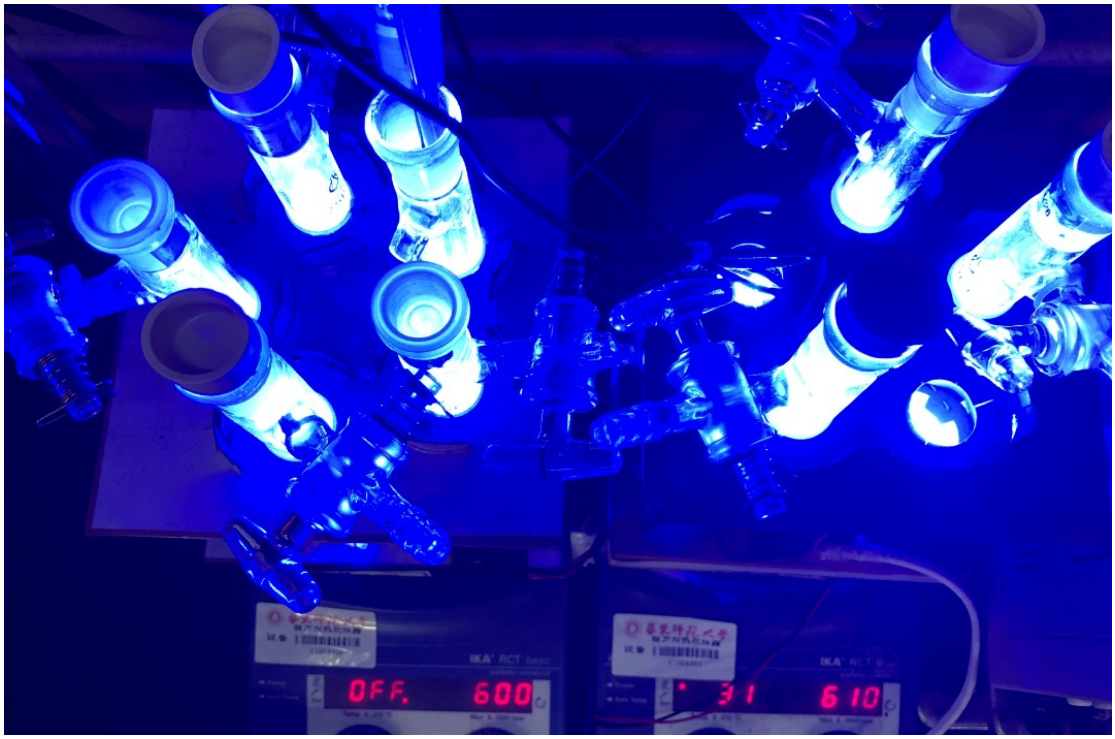
## 1) The General Procedure



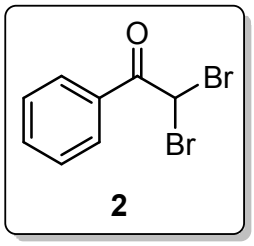

Condition **A**: In a Schlenk tube, **Substrate** (0.2 mmol, 1.0 equiv.), NaBr (0.5 mmol, 2.5 equiv.), $NaHSO_4 \cdot H_2O$ (0.7 mmol, 3.5 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), and the reaction mixture was stirred under 2 W*3 blue LEDs at room temperature for 8 hours, which is opened to air. After the reaction completed, the reaction mixture was purified by column chromatography on silica gel to give desired product.

Condition **B**: In a Schlenk tube, **Substrate** (0.2 mmol, 1.0 equiv.), LiCl (0.6 mmol, 3.0 equiv.), $NaHSO_4 \cdot H_2O$ (0.8 mmol, 4.0 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), and the reaction mixture was stirred under 6 W blue LEDs at room temperature for 24 hours, which is opened to air. After the reaction completed, the reaction mixture was purified by column chromatography on silica gel to give desired product.


HSPY-120-01
097.6V 097.6V CV
0.557A 0.700A ON
U/I
Stop/Run
9.0 cm
8.5 cm
IKA RCT basic
safety control
OFF 600
31 610


OFF 600
31 610

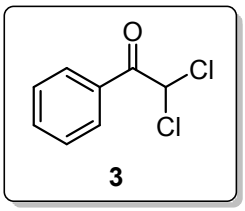
**2) The Procedure and Data of Table 1 and 2**



**2**

**2,2-dibromo-1-phenylethan-1-one 2:** Prepared under outlined condition **A** as in general procedure using ethynylbenzene (20.4 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), $NaHSO_4 \cdot H_2O$ (96.7 mg, 3.5 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound **2**[2] in 85% (47.1 mg) yield as yellow oil. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.09 – 8.07 (m, 2H), 7.65 – 7.62 (m, 1H), 7.53 – 7.49 (m, 2H), 6.71 (s, 1H)； **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 185.98, 134.47, 130.88, 129.72, 128.96, 39.71； **MS (EI)** m/z 276; **IR** (film) 1693, 1593, 1579, 1448, 1267, 1190, 979, 800, 702, 682, 626, 570 $cm^{-1}$.

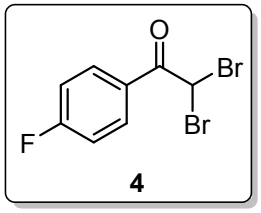
Prepared under outlined condition **A** as in general procedure using ethynylbenzene (2.04 g, 2.0 mmol, 1.0 equiv.), NaBr (5.14 mg, 2.5 equiv.), $NaHSO_4 \cdot H_2O$ (9.67 mg, 3.5 equiv.), $H_2O$ (1.08 g, 30.0 equiv.) were dissolved in $CH_3CN$ (80 mL), the reaction was stirred under 2 W *15 blue LEDs at room temperature for 48 hours with bubbling oxygen using balloon affording compound **2**[2] in 56% (3.113 g) yield as yellow oil.



**3**

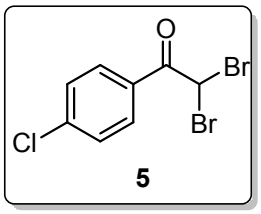
**2,2-dichloro-1-phenylethan-1-one 3:** Prepared under outlined condition **B** as in general procedure using ethynylbenzene (20.4 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), $NaHSO_4 \cdot H_2O$ (110.4 mg, 4.0 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound **3**[2] in 63% (24.1 mg) yield as colorless oil. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.17 – 8.01 (m, 2H), 7.65 (dt, $J$ = 8.7, 1.2 Hz, 1H), 7.58 – 7.47 (m, 2H), 6.69 (s, 1H)； **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 185.92, 134.57, 131.36, 129.76, 128.93, 67.80; **HRMS (ESI)** $[M+Na]^+$ Calcd for $C_8H_6Cl_2ONa$ 210.9693, Found 210.9986; **IR** (film) 2920, 2850, 1707, 1647, 1469, 1363, 1259, 1082, 1022, 968, 802,

567 $cm^{-1}$.



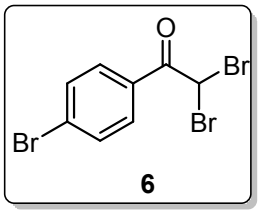
**4**

**2,2-dibromo-1-(4-fluorophenyl)ethan-1-one 4**: Prepared under outlined condition **A** as in general procedure using 1-ethynyl-4-fluorobenzene (24.0 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), $NaHSO_4{\cdot}H_2O$ (96.7 mg, 3.5 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound **4**[2] in 72% (42.3 mg) yield as pale yellow oil. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.17 – 8.12 (m, 2H), 8.20 – 8.16 (m, 2H), 6.62 (s, 1H)； **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 184.57, 166.35 (d, *J* = 258.9 Hz), 132.69 (d, *J* = 9.5 Hz), 127.11 (d, *J* = 2.9 Hz), 116.24 (d, *J* = 9.5 Hz), 39.36； **$^{19}$F NMR (282 MHz, $CDCl_3$)** δ -101.83 – -101.91 (m)； **MS (EI)** m/z 294; **IR** (film) 1697, 1597, 1506, 1413, 1271, 1242, 1190, 1161, 983, 850, 765, 704, 588 $cm^{-1}$.



**5**

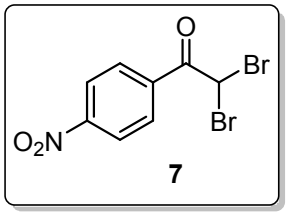
**2,2-dibromo-1-(4-chlorophenyl)ethan-1-one 5:** Prepared under outlined condition **A** as in general procedure using 1-chloro-4-ethynylbenzene (27.3 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), $NaHSO_4{\cdot}H_2O$ (96.7 mg, 3.5 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound **5**[2] in 74% (45.8 mg) yield as pale yellow oil. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.05 (d, *J* = 7.9 Hz, 2H), 7.49 (d, *J* = 7.9 Hz, 2H), 6.61 (s, 1H)； **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 184.91, 141.08, 131.22, 129.30, 129.10, 39.24； **MS (EI)** m/z 310; **IR** (film) 3037, 1693, 1587, 1402, 1276, 1205, 1093, 989, 844, 765, 729, 665, 565 $cm^{-1}$.



**6**

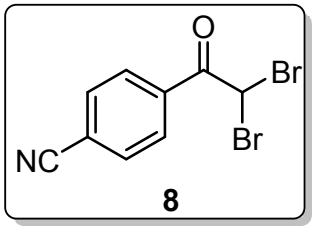
**2,2-dibromo-1-(4-bromophenyl)ethan-1-one 6:** Prepared

under outlined condition **A** as in general procedure using 1-bromo-4-ethynylbenzene (36.2 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), $NaHSO_4 \cdot H_2O$ (96.7 mg, 3.5 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound **6**[2] in 88% (62.6 mg) yield as white solid. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.00 – 7.94 (m, 2H), 7.69 – 7.61 (m, 2H), 6.61 (s, 1H)；**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 185.12, 132.31, 131.24, 129.91, 129.53，39.26；**MS (EI)** m/z 356; **IR** (film) 3034, 1693, 1581, 1485, 1394, 1271, 1201, 1070, 985, 840, 719, 653, 563 $cm^{-1}$.



**7**

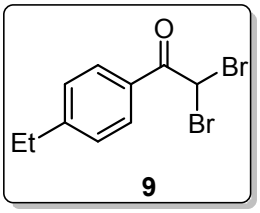
**2,2-dibromo-1-(4-nitrophenyl)ethan-1-one 7:** Prepared under outlined condition **A** as in general procedure using 1-ethynyl-4-nitrobenzene (29.4 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), $NaHSO_4 \cdot H_2O$ (96.7 mg, 3.5 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound **7**[3] in 56% (35.9 mg) yield as yellow solid. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.35 (d, *J* = 8.9 Hz, 2H), 8.30 (d, *J* = 8.7 Hz, 2H), 6.60 (s, 1H)；**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 184.52, 150.83, 135.63, 131.04, 123.95，38.78；**MS (EI)** m/z 321; **IR** (film) 2920, 1705, 1600, 1521, 1344, 1259, 1190, 987, 866, 854, 785, 713, 657, 565 $cm^{-1}$.



**8**

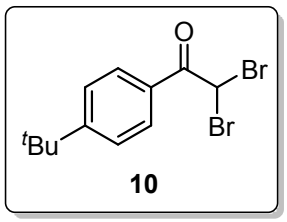
**2,2-dibromo-1-(4-cyanophenyl)ethan-1-one 8:** Prepared under outlined condition **A** as in general procedure using 4-cyanobenzonitrile (25.4 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), $NaHSO_4 \cdot H_2O$ (96.7 mg, 3.5 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound **8**[4] in 82% (49.3 mg) yield as white solid. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.26 – 8.16 (m,

2H), 7.85 – 7.77 (m, 2H), 6.59 (s, 1H); **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 184.73, 134.11, 132.93, 132.61, 130.29, 117.53, 38.83; **MS (EI)** m/z 301; **IR** (film) 2920, 2231, 1703, 1404, 1261, 1205, 989, 852, 761, 680, 574 $cm^{-1}$.



**9**

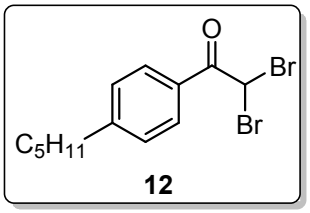
**2,2-dibromo-1-(4-ethylphenyl)ethan-1-one 9:** Prepared under outlined condition **A** as in general procedure using 1-ethyl-4-ethynylbenzene (26.0 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), $NaHSO_4{\cdot}H_2O$ (96.7 mg, 3.5 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound **9**[5] in 80% (48.6 mg) yield as colorless oil. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.01 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.71 (s, 1H), 2.73 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H); **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 185.66, 151.83, 129.96, 128.49, 128.40, 39.92, 29.08, 15.02; **MS (EI)** m/z 304; **IR** (film) 2966, 1691, 1604, 1415, 1271, 1182, 981, 848, 686, 761, 592, 570 $cm^{-1}$.



**10**

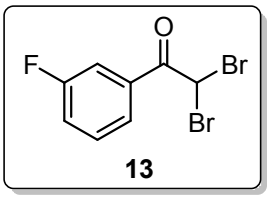
**2,2-dibromo-1-(4-(*tert*-butyl)phenyl)ethan-1-one 10:** Prepared under outlined condition **A** as in general procedure using 1-(*tert*-butyl)-4-ethynylbenzene (31.7 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), $NaHSO_4{\cdot}H_2O$ (96.7 mg, 3.5 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8[6] hours affording compound **10**[6] in 76% (50.4 mg) yield as colorless oil. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.03 (d, *J* = 8.6 Hz, 2H), 7.52 (d, *J* = 8.6 Hz, 2H), 6.71 (s, 1H), 1.35 (s, 9H); **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 185.61, 158.61, 129.75, 128.11, 125.98, 39.93, 35.37, 31.01; **MS (EI)** m/z 332; **IR** (film) 2962, 1693, 1602, 1408, 1363. 1267, 1190, 1105, 981, 848, 709, 667, 576, 563 $cm^{-1}$.

**1-([1,1'-biphenyl]-4-yl)-2,2-dibromoethan-1-one 11:** Prepared under outlined condition A as in general procedure using 4-ethynyl-1,1'-biphenyl (35.7 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), $NaHSO_4 \cdot H_2O$ (96.7 mg, 3.5 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound **11**[3] in 72% (50.7 mg) yield as white solid. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.17 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.46 (dt, *J* = 24.6, 7.3 Hz, 3H), 6.74 (s, 1H)； **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 185.59, 147.18, 139.37, 130.38, 129.43, 129.09, 128.70, 127.52, 127.34, 39.82； **MS (EI)** m/z 352; **IR** (film) 1693, 1600, 1406, 1269, 1190, 983, 854, 779, 746, 694, 624, 570 $cm^{-1}$.



**12**

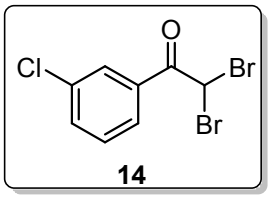
**2,2-dibromo-1-(4-pentylphenyl)ethan-1-one 12:** Prepared under outlined condition A as in general procedure using 1-ethynyl-4-pentylbenzene (34.6 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), $NaHSO_4 \cdot H_2O$ (96.7 mg, 3.5 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound **12**[7] in 56% (38.7 mg) yield as colorless oil. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.70 (s, 1H), 2.68 (t, *J* = 7.7 Hz, 2H), 1.72 – 1.60 (m, 2H), 1.33 (d, J = 3.4 Hz, 4H), 0.90 (t, J = 6.6 Hz, 3H)； 13C NMR **(101 MHz, $CDCl_3$)** δ 185.66, 150.66, 129.87, 129.01, 128.38, 39.87, 36.10, 31.43, 30.64, 22.48, 13.98； **MS (EI)** m/z 346; **IR** (film) 2927, 1693, 1602, 1415, 1269, 1182, 983, 852, 690, 596, 570 $cm^{-1}$.



**13**

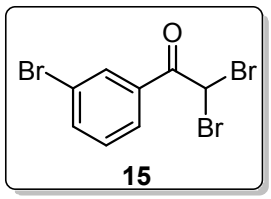
**2,2-dibromo-1-(3-fluorophenyl)ethan-1-one 13:** Prepared under outlined condition A as in general procedure using 1-

ethynyl-3-fluorobenzene (24.0 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), $NaHSO_4 \cdot H_2O$ (96.7 mg, 3.5 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound **13**[8] in 86% (51.7 mg) yield as colorless oil. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.88 (d, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 9.3 Hz, 1H), 7.50 (dd, *J* = 13.8, 7.8 Hz, 1H), 7.34 (t, *J* = 8.2 Hz, 1H), 6.63 (s, 1H)；**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 184.85 (d, *J* = 2.4 Hz), 162.71 (d, *J* = 249.97 Hz), 132.81 (d, *J* = 6.7 Hz), 130.61 (d, *J* = 7.7 Hz) , 125.47 (d, *J* = 3.1 Hz), 121.58 (d, *J* = 21.5 Hz), 116.70 (d, *J* = 23.2 Hz), 39.14；**$^{19}$F NMR (282 MHz, $CDCl_3$)** δ -101.83 – -101.91 (m)；**MS (EI)** m/z 294; **IR** (film) 1697, 1587, 1485, 1438, 1267, 1153, 875, 752, 700, 671, 624, 582 $cm^{-1}$.



**14**

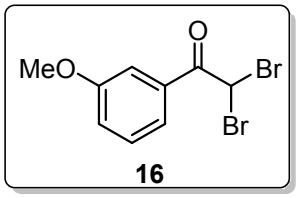
**2,2-dibromo-1-(3-chlorophenyl)ethan-1-one 14:** Prepared under outlined condition A as in general procedure using 1-chloro-3-ethynylbenzene (27.3 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), $NaHSO_4 \cdot H_2O$ (96.7 mg, 3.5 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound **14**[8]in 74% (46.2 mg) yield as pale yellow oil. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.06 (t, *J* = 1.7 Hz, 1H), 7.98 (dd, *J* = 7.9, 0.6 Hz, 1H), 7.65 – 7.57 (m, 1H), 7.46 (t, *J* = 7.9 Hz, 1H), 6.62 (s, 1H)；**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 184.84, 135.30, 134.38, 132.42, 130.19, 129.76, 127.79, 39.13；**MS (EI)** m/z 312; **IR** (film) 1699, 1570, 1471, 1419, 1253, 1190, 1091, 1076, 798, 736, 669, 624, 572 $cm^{-1}$.



**15**

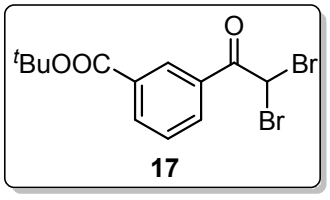
**2,2-dibromo-1-(3-bromophenyl)ethan-1-one 15:** Prepared under outlined condition A as in general procedure using 1-

bromo-3-ethynylbenzene (36.2 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), $NaHSO_4 \cdot H_2O$ (96.7 mg, 3.5 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound **15**[6] in 76% (53.7 mg) yield as yellow oil. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.21 (s, 1H), 8.07 – 7.98 (m, 1H), 7.81 – 7.74 (m, 1H), 7.40 (t, *J* = 7.9 Hz, 1H), 6.61 (s, 1H)； **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 184.73, 137.28, 132.67, 132.61, 130.40, 128.22, 123.19, 39.04； **MS (EI)** m/z 354; **IR** (film) 1699,1566, 1471, 1419, 1251, 1190, 1068, 993, 800, 731, 671, 624, 572 $cm^{-1}$.



**16**

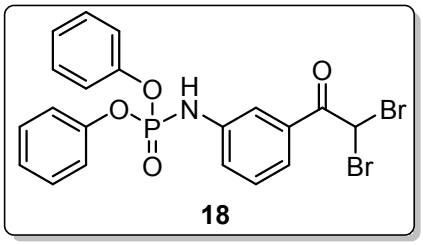
**2,2-dibromo-1-(3-methoxyphenyl)ethan-1-one 16:** Prepared under outlined condition A as in general procedure using 1-ethynyl-3-methoxybenzene (26.4 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), $NaHSO_4 \cdot H_2O$ (96.7 mg, 3.5 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound **16** in 86% (52.6 mg) yield as white solid. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.64 (d, *J* = 8.3 Hz, 1H), 7.60 – 7.55 (m, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.17 (dd, *J* = 8.3, 2.6 Hz, 1H), 6.71 (s, 1H), 3.87 (s, 3H)； **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 185.88, 160.01, 132.13, 129.88, 121.96, 121.06, 114.08, 55.57, 39.65; **HRMS (EI)** m/z Calcd for $C_9H_8Br_2O_2$ 305.8891, Found 305.8894; **IR** (film) 1693, 1595, 1581, 1485,1427, 1271, 1161, 1041, 875, 798, 748, 677, 626, 588 $cm^{-1}$.



**17**

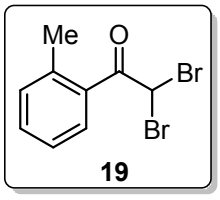
***tert*-butyl 3-(2,2-dibromoacetyl)benzoate 17:** Prepared under outlined condition A as in general procedure using *tert*-butyl 3-ethynylbenzoate (40.5 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5

equiv.), $NaHSO_4{\cdot}H_2O$ (96.7 mg, 3.5 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound **17** in 54% (40.7 mg) yield as colorless oil. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.67 (t, *J* = 1.6 Hz, 1H), 8.29 – 8.19 (m, 2H), 7.58 (t, *J* = 7.8 Hz, 1H), 6.71 (s, 1H), 1.62 (s, 9H)； **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 185.45, 164.37, 134.96, 133.32, 132.93, 131.04, 130.57, 129.02, 82.11, 39.36, 28.17； **HRMS (ESI)** $[M+Na]^+$ Calcd for $C_{13}H_{14}Br_2O_3Na$ 398.9207，Found 398.9227; **IR** (film) 2978, 1701, 1602, 1367, 1309, 1247, 1155, 846, 779, 732, 677, 634, 570 $cm^{-1}$.



**18**

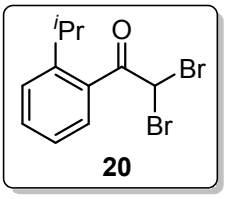
**diphenyl (3-(2,2-dibromoacetyl)phenyl)phosphoramidate 18:** Prepared under outlined condition A as in general procedure using diphenyl (3-ethynylphenyl)phosphoramidate (69.9 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), $NaHSO_4{\cdot}H_2O$ (96.7 mg, 3.5 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound **18** in 72% (75.2 mg) yield as white solid. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.00 (d, *J* = 10.4 Hz, 1H), 7.87 (d, *J* = 1.9 Hz, 1H), 7.67 (dt, *J* = 7.2, 1.6 Hz, 1H), 7.40 – 7.30 (m, 2H), 7.28 – 7.21 (m, 4H), 7.21 – 7.15 (m, 4H), 7.12 (dd, *J* = 11.0, 4.0 Hz, 2H), 6.63 (s, 1H)； **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 185.73, 150.15, 150.09, 140.11, 131.91, 129.89, 125.59, 123.98, 123.90, 123.29, 120.29, 120.25, 118.81, 118.74, 39.74； **$^{31}$P NMR (122 MHz, $CDCl_3$)** δ -7.30 (d, *J* = 9.7 Hz)； **HRMS (ESI)** $[M+Na]^+$ Calcd for $C_{20}H_{16}Br_2NO_4PNa$ 545.9081，Found 545.9067; **IR** (film) 1699, 1589, 1489, 1296, 1184, 1161, 979, 948, 763, 688, 628, 586 $cm^{-1}$.



**19**

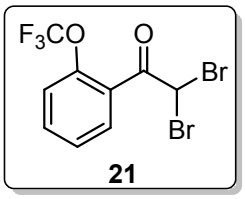
**2,2-dibromo-1-(*o*-tolyl)ethan-1-one 21:** Prepared under outlined condition A as in general procedure using 1-ethynyl-2-

methylbenzene (23.2 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), $NaHSO_4 \cdot H_2O$ (96.7 mg, 3.5 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound **21**[6] in 84% (49.0 mg) yield as colorless oil. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.71 – 7.64 (m, 1H), 7.45 (td, *J* = 7.6, 1.1 Hz, 1H), 7.36 – 7.26 (m, 2H), 6.68 (s, 1H), 2.51 (s, 3H)；**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 188.58, 140.26, 132.71, 132.30, 136.26, 128.10, 125.77, 42.23, 21.10；**MS (EI)** m/z 292; **IR** (film) 1699, 1598, 1570, 1456, 1253, 1178, 968, 792, 736, 632, 572 cm$^{-1}$.



**20**

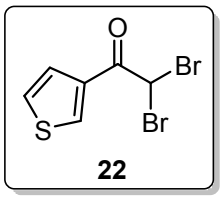
**2,2-dibromo-1-(2-isopropylphenyl)ethan-1-one 22:** Prepared under outlined condition A as in general procedure using 1-ethynyl-2-isopropylbenzene (28.9 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), $NaHSO_4 \cdot H_2O$ (96.7 mg, 3.5 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound **22** in 84% (53.4 mg) yield as colorless oil. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.53 – 7.45 (m, 3H), 7.24 (ddd, *J* = 8.2, 6.0, 1.8 Hz, 1H), 6.59 (s, 1H), 3.20 (dt, *J* = 13.6, 6.8 Hz, 1H), 1.28 (s, 3H), 1.26 (s, 3H).；**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 189.93, 149.63, 133.07, 132.39, 127.07, 126.70, 125.55, 43.02, 30.19, 24.28；**HRMS (EI)** m/z Calcd for $C_{11}H_{12}Br_2O$ 317.9255, Found 239.0064 [M–·Br]; **IR** (film) 2964, 1707, 1598, 1444, 1249, 1176, 972, 790, 758, 692, 630, 574 cm$^{-1}$.



**21**

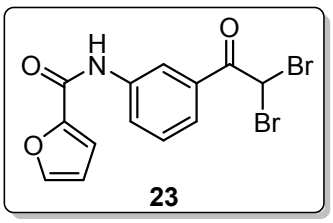
**2,2-dibromo-1-(2-(trifluoromethoxy)phenyl)ethan-1-one 23:** Prepared under outlined condition A as in general procedure using 1-ethynyl-2-(trifluoromethoxy)benzene (37.2 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), $NaHSO_4 \cdot H_2O$ (96.7 mg, 3.5 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6

W blue LEDs at room temperature for 8 hours affording compound **23** in 56% (40.3 mg) yield as colorless oil. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.82 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.63 (ddd, *J* = 8.4, 7.5, 1.8 Hz, 1H), 7.43 (td, *J* = 7.6, 1.0 Hz, 1H), 7.40 – 7.34 (m, 1H), 6.72 (s, 1H)；**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 186.71, 146.50 (d, J = 1.6 Hz), 134.35, 131.97, 127.29, 127.07, 120.66 (d, *J* = 1.6 Hz), 120.25 (q, *J* = 260.8 Hz), 42.05；**$^{19}$F NMR (282 MHz, $CDCl_3$)** δ -57.03 (d, *J* = 1.5 Hz)；**HRMS (EI)** m/z Calcd for $C_{11}H_{12}Br_2O$ 317.9255, Found 239.0064 [M–Br]; **IR** (film) 1714, 1602, 1450, 1247, 1161, 983, 923, 781, 758, 630, 617 $cm^{-1}$.



**22**

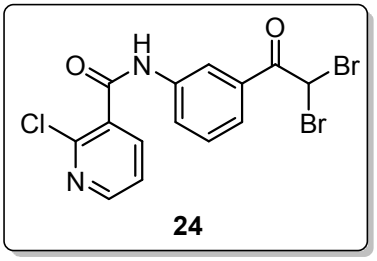
**2,2-dibromo-1-(thiophen-3-yl)ethan-1-one 20:** Prepared under outlined condition A as in general procedure using 3-ethynylthiophene (21.6 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), $NaHSO_4{\cdot}H_2O$ (96.7 mg, 3.5 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 2 hours affording compound **20**[2] in 64% (36.4 mg) yield as brown yellow oil. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.37 (dd, *J* = 2.8, 1.0 Hz, 1H), 7.67 (d, *J* = 5.1 Hz, 1H), 7.37 (dd, *J* = 5.1, 2.9 Hz, 1H), 6.43 (d, *J* = 0.8 Hz, 1H)；**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 180.56, 135.34, 134.57, 128.03, 126.80, 40.22；**MS (EI)** m/z 282; **IR** (film) 1681, 1504, 1409, 1257, 1176, 999, 812, 742, 667, 605$cm^{-1}$.



**23**

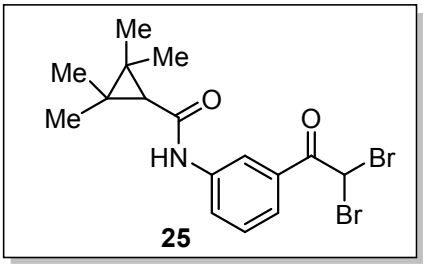
***N*-(3-(2,2-dibromoacetyl)phenyl)furan-2-carboxamide 24:** Prepared under outlined condition A as in general procedure using *N*-(3-ethynylphenyl)furan-2-carboxamide (42.2 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), $NaHSO_4{\cdot}H_2O$ (96.7 mg, 3.5 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound **24** in 61% (47.7 mg) yield as white solid.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.35 (t, *J* = 1.8 Hz, 1H), 8.28 (s, 1H), 8.07 – 7.96 (m, 1H), 7.89 – 7.81 (m, 1H), 7.58 – 7.47 (m, 2H), 7.28 (d, *J* = 3.5 Hz, 1H), 6.74 (s, 1H), 6.58 (dd, *J* = 3.5, 1.7 Hz, 1H)；**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 185.67, 156.29, 147.27, 144.63, 138.25, 131.72, 129.79, 125.64, 125.49, 120.62, 116.01, 112.85, 39.57；**HRMS (ESI)** $[M+H]^+$ Calcd for $C_{13}H_{10}Br_2NO_3$ 385.9027，Found 385.9030; **IR** (film) 1697, 1662, 1581, 1539, 1433, 1313, 1267, 1161, 1012, 883, 806, 754, 678, 628, 592 $cm^{-1}$.



**24**

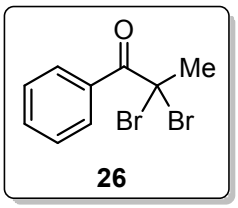
**2-chloro-*N*-(3-(2,2-dibromoacetyl)phenyl)nicotinamide 25:** Prepared under outlined condition A as in general procedure using 2-chloro-*N*-(3-ethynylphenyl)nicotinamide (51.3 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), $NaHSO_4{\cdot}H_2O$ (96.7 mg, 3.5 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound **25** in 79% (68.2 mg) yield as white solid. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.81 (s, 1H), 8.44 (dd, *J* = 4.8, 1.9 Hz, 1H), 8.29 (d, *J* = 1.6 Hz, 1H), 8.08 (dd, *J* = 7.6, 1.9 Hz, 1H), 8.02 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.91 – 7.81 (m, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.35 (dd, *J* = 7.6, 4.8 Hz, 1H), 6.72 (s, 1H)；**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 185.76, 163.37, 151.39, 147.10, 139.56, 138.22, 131.72, 131.29, 129.86, 126.17, 126.10, 122.95, 121.08, 39.55；**HRMS (ESI)** $[M+H]^+$ Calcd for $C_{14}H_{10}Br_2ClN_2O_2$ 430.8798，Found 430 8788; **IR** (film) 1662, 1579, 1546, 1487, 1433, 1398, 1271, 1138, 1066, 736, 678, 628 $cm^{-1}$.



**25**

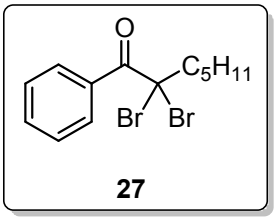
***N*-(3-(2,2-dibromoacetyl)phenyl)-2,2,3,3-tetramethylcyclopropane-1-carboxamide 19:** Prepared under outlined condition A as in general

procedure using *N*-(3-ethynylphenyl)-2,2,3,3-tetramethylcyclopropane-1-carboxamide (48.3 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), $NaHSO_4 \cdot H_2O$ (96.7 mg, 3.5 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at ro om temperature for 8 hours affording compound **19** in 83% (68.1 mg) yield as white solid. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.08 (t, *J* = 1.8 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.76 – 7.59 (m, 2H), 7.40 (t, *J* = 8.0 Hz, 1H), 6.74 (s, 1H), 1.32 (s, 6H), 1.21 (s, 6H)；**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 186.00, 170.63, 139.36, 131.48, 129.53, 125.67, 124.51, 120.10, 39.76, 38.50, 30.09, 23.78, 16.71；**HRMS (ESI)** $[M+Na]^+$ Calcd for $C_{16}H_{19}Br_2NO_2Na$ 437.9680，Found 437.9678; **IR** (film) 2945, 1660,1591, 1541, 1487, 1431, 1300, 1155, 1112, 806, 702, 628 $cm^{-1}$.



**26**

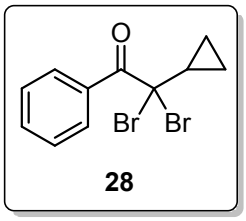
**2,2-dibromo-1-phenylpropan-1-one 26:** Prepared under outlined condition A as in general procedure using prop-1-yn-1-ylbenzene (23.2 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), $NaHSO_4 \cdot H_2O$ (96.7 mg, 3.5 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound **26**[2] in 83% (48.5 mg) yield as colorless oil. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.41 (d, *J* = 7.6 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 2.76 (s, 3H)；**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 188.30, 133.50, 131.74, 131.38, 127.98, 57.95, 37.75；**MS (EI)** m/z 292; **IR** (film) 1680, 1595, 1446, 1377, 1249, 1186, 1062, 952, 800, 717, 684, 650, 574 $cm^{-1}$.



**27**

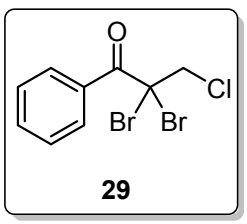
**2,2-dibromo-1-phenylheptan-1-one 27:** Prepared under outlined condition A as in general procedure using hept-1-yn-1-ylbenzene (34.5 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), $NaHSO_4 \cdot H_2O$ (96.7 mg, 3.5 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were

dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound **27** in 76% (52.5 mg) yield as colorless oil. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.34 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 2.71 – 2.63 (m, 2H), 1.79 – 1.68 (m, 2H), 1.49 – 1.32 (m, 4H), 0.93 (t, *J* = 6.8 Hz, 3H)； **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 188.65, 133.19, 132.76, 131.07, 127.91, 67.02, 46.80, 31.17, 27.09, 22.44, 13.97； **HRMS (EI)** m/z Calcd for $C_{13}H_{16}Br_2O$ 345.9568, Found 267.0380 [M–Br]; **IR** (film) 2929, 1680, 1597, 1446, 1232, 1186, 974, 810, 711, 686, 655, 607, 570 $cm^{-1}$.



**28**

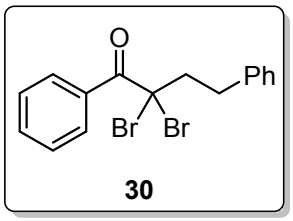
**2,2-dibromo-2-cyclopropyl-1-phenylethan-1-one 28:** Prepared under outlined condition A as in general procedure using (cyclopropylethynyl)benzene (28.4 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), $NaHSO_4{\cdot}H_2O$ (96.7 mg, 3.5 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound **28** in 57% (35.8 mg) yield as colorless oil. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.35 (d, *J* = 7.8 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 2.01 – 1.85 (m, 1H), 0.99 – 0.83 (m, 4H)； **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 188.43, 133.12, 132.87, 131.09, 127.92, 71.35, 25.35, 7.58； **HRMS (EI)** m/z Calcd for $C_{11}H_{10}Br_2O$ 315.9098, Found 315.9096; **IR** (film) 1680, 1595, 1446, 1232, 1136, 1022, 947, 839, 804. 736, 686, 653, 613 $cm^{-1}$.



**29**

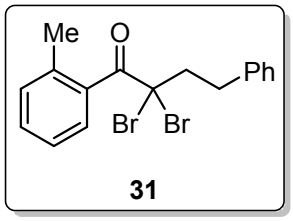
**2,2-dibromo-3-chloro-1-phenylpropan-1-one 29:** Prepared under outlined condition A as in general procedure using (3-chloroprop-1-yn-1-yl)benzene (30.1 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), $NaHSO_4{\cdot}H_2O$ (96.7 mg, 3.5 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was

stirred under 6 W blue LEDs at room temperature for 8 hours affording compound **29**[8] in 68% (44.1 mg) yield as white solid. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.31 (d, *J* = 7.6 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 4.49 (s, 2H)； **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 186.97, 133.78, 132.00, 130.93, 128.12, 60.91, 53.68； **MS (EI)** m/z 324; **IR** (film) 1685, 1678, 1595, 1446, 1251, 1186, 935, 817, 767, 686, 607, 586 $cm^{-1}$.



**30**

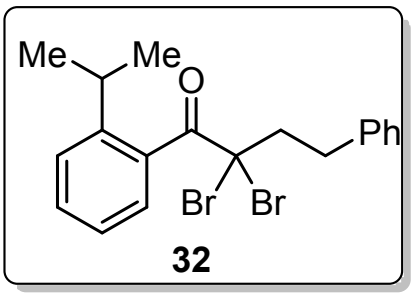
**2,2-dibromo-1,4-diphenylbutan-1-one 30:** Prepared under outlined condition A as in general procedure using but-1-yne-1,4-diyldibenzene (41.2 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), $NaHSO_4{\cdot}H_2O$ (96.7 mg, 3.5 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound **30** in 63% (48.0 mg) yield as white solid. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.41 (d, *J* = 7.8 Hz, 2H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.38 – 7.33 (m, 2H), 7.29 (dd, *J* = 12.8, 8.2 Hz, 3H), 3.12 – 3.05 (m, 2H), 3.05 – 2.98 (m, 2H)； **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 188.36, 140.25, 133.40, 132.53, 131.16, 128.70, 128.62, 128.01, 126.36, 65.47, 48.81, 33.89； **HRMS (ESI)** $[M+Na]^+$ Calcd for $C_{16}H_{14}Br_2ONa$ 402.9309, Found 402.9316; **IR** (film) 2920, 2850, 1728, 1645, 1469, 1261, 1080, 966, 800, 700 $cm^{-1}$.



**31**

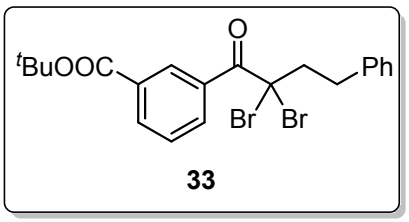
**2,2-dibromo-4-phenyl-1-(*o*-tolyl)butan-1-one 31:** Prepared under outlined condition A as in general procedure using 1-methyl-2-(4-phenylbut-1-yn-1-yl)benzene (44.1mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), $NaHSO_4{\cdot}H_2O$ (96.7 mg, 3.5 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was

stirred under 6 W blue LEDs at room temperature for 8 hours affording compound **31** in 72% (56.7 mg) yield as colorless oil. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.01 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.30 (td, *J* = 7.6, 1.3 Hz, 1H), 7.27 – 7.12 (m, 7H), 2.96 – 2.85 (m, 4H), 2.28 (s, 3H)；**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 194.26, 139.97, 137.37, 135.97, 131.22, 130.81, 128.67, 128.66, 128.18, 126.47, 124.97, 67.78, 48.44, 34.03, 20.57；**HRMS (EI)** m/z Calcd for $C_{17}H_{16}Br_2O$ 393.9568, Found 315.0377 [M–Br]; **IR** (film) 1695, 1600, 1496, 1454, 1234, 808, 748, 725, 698, 563 $cm^{-1}$.



**32**

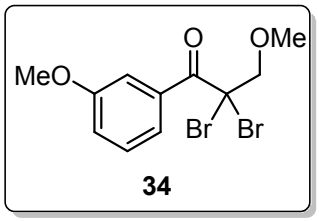
**2,2-dibromo-1-(2-isopropylphenyl)-4-phenylbutan-1-one 32:** Prepared under outlined condition A as in general procedure using 1-isopropyl-2-(4-phenylbut-1-yn-1-yl)benzene (49.7 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), $NaHSO_4{\cdot}H_2O$ (96.7 mg, 3.5 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound **32** in 68% (57.4 mg) yield as colorless oil. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.86 – 7.74 (m, 1H), 7.42 – 7.31 (m, 2H), 7.29 – 7.20 (m, 2H), 7.20 – 7.10 (m, 4H), 3.02 – 2.91 (m, 2H), 2.88 (ddd, *J* = 10.0, 5.4, 2.2 Hz, 2H), 2.78 (hept, *J* = 6.8 Hz, 1H), 1.19 (d, *J* = 6.8 Hz, 6H)；**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 195.76, 147.35, 139.88, 135.99, 130.69, 128.69, 128.66, 127.27, 126.49, 126.17, 125.03, 68.41, 48.19, 33.98, 31.47, 24.21; **HRMS (EI)** m/z Calcd for $C_{19}H_{20}Br_2O$ 421.9881, Found 343.0698 [M–Br]; **IR** (film) 2964, 1699, 1496, 1454, 1234, 1201, 1033, 943, 758, 698, 653, 624 $cm^{-1}$.



**33**

***tert*-butyl 3-(2,2-dibromo-4-phenylbutanoyl)benzoate 33:** Prepared under outlined condition A as in general procedure using

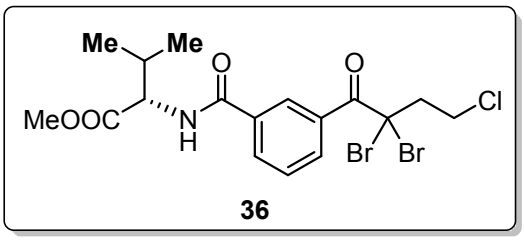
*tert*-butyl 3-(4-phenylbut-1-yn-1-yl)benzoate (61.3 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), $NaHSO_4 \cdot H_2O$ (96.7 mg, 3.5 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound **33** in 54% (51.9 mg) yield as colorless oil. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.99 (s, 1H), 8.54 (d, *J* = 7.9 Hz, 1H), 8.20 (d, *J* = 7.7 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.36 – 7.21 (m, 5H), 3.08 – 3.05 (m, 2H), 3.01 – 2.98 (m, 2H), 1.63 (s, 9H)；**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 187.74, 164.70, 140.14, 134.65, 133.95, 132.69, 132.18, 132.11, 128.68, 128.63, 128.01, 126.38, 81.79, 65.09, 48.63, 33.85, 28.20；**HRMS (ESI)** $[M+Na]^+$ Calcd for $C_{21}H_{22}Br_2O_3Na$ 502.9833，Found 502.9855; **IR** (film) 1714, 1683, 1600, 1454, 1367, 1307, 1224, 1157, 1124, 848, 729, 698, 615, 578 $cm^{-1}$.



**34**

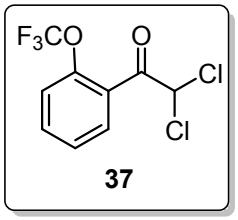
**2,2-dibromo-3-methoxy-1-(3-methoxyphenyl)propan-1-one 34:** Prepared under outlined condition A as in general procedure using 1-methoxy-4-(3-methoxyprop-1-yn-1-yl)benzene (54.8 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), $NaHSO_4 \cdot H_2O$ (96.7 mg, 3.5 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound **34** in 86% (48.5 mg) yield as colorless oil. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.95 (d, *J* = 7.8 Hz, 1H), 7.77 (s, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 1H), 4.22 (s, 2H), 3.85 (s, 3H), 3.56 (s, 3H)；**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 187.71, 159.12, 133.61, 128.93, 123.40, 119.88, 115.47, 79.85, 61.45, 59.94, 55.46；**HRMS (ESI)** $[M+Na]^+$ Calcd for $C_{11}H_{12}Br_2O_3Na$ 372.9051，Found 372.9071; **IR** (film) 1678, 1579, 1487, 1425, 1261, 1211, 1126, 1035, 810, 750, 682, 636, 596 $cm^{-1}$.

**2-(2,2-dibromo-4-chlorobutanoyl)benzyl 2,2-dichloroacetate 35:** Prepared under outlined condition A as in general procedure using 2-(4-chlorobut-1-yn-1-yl)benzyl 2,2-dichloroacetate (61.1 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), $NaHSO_4 \cdot H_2O$ (96.7 mg, 3.5 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound **35** in 68% (65.1 mg) yield as colorless oil. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.48 (d, *J* = 7.8 Hz, 1H), 7.63 – 7.55 (m, 2H), 7.48 – 7.42 (m, 1H), 5.98 (s, 1H), 5.43 (s, 2H), 3.93 – 3.86 (m, 2H), 3.22 – 3.14 (m, 2H)；**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 191.11, 164.01, 135.52, 133.14, 132.49, 130.22, 129.78, 127.77, 66.65, 64.13, 61.92, 48.69, 41.28；**HRMS (ESI)** $[M+Na]^+$ Calcd for $C_{11}H_8Br_2Cl_2O_2Na$ 500.8038，Found 500.8032; **IR** (film) 2924, 1768, 1724, 1602, 1465, 1288, 1155, 1029, 763, 727 $cm^{-1}$.



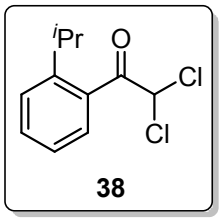

**methyl (3-(2,2-dibromo-4-chlorobutanoyl)benzoyl)-*L*-valinate 36:** Prepared under outlined condition A as in general procedure using methyl (3-(4-chlorobut-1-yn-1-yl)benzoyl)-*L*-valinate (64.4 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), $NaHSO_4 \cdot H_2O$ (96.7 mg, 3.5 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound **36** in 51% (50.9 mg) yield as colorless syrup. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.73 (s, 1H), 8.53 (d, *J* = 7.8 Hz, 1H), 8.03 (d, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 1H), 6.73 (d, *J* = 8.1 Hz, 1H), 4.78 (dd, *J* = 8.3, 5.0 Hz, 1H), 3.94 – 3.84 (m, 2H), 3.78 (s, 4H), 3.23 – 3.14 (m, 2H), 2.30 (dq, *J* = 12.5, 6.4 Hz, 1H), 1.01 (t, *J* = 7.2 Hz, 6H)；**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 186.74, 172.49, 166.08, 134.38, 134.13, 132.20, 131.95, 129.70, 128.50, 60.51, 57.62, 52.37, 49.03,

41.30, 31.61, 19.03, 17.98; **HRMS (ESI)** $[M+Na]^+$ Calcd for $C_{17}H_{20}Br_2ClNO_4Na$ 517.9345, Found 517.9349; **IR** (film) 2962, 1739, 1645, 1529, 1228, 1155, 1001, 821, 682, 588 $cm^{-1}$.



**37**

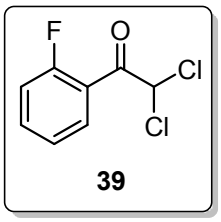
**2,2-dichloro-1-(2-(trifluoromethoxy)phenyl)ethan-1-one 37:** Prepared under outlined condition B as in general procedure using 1-ethynyl-2-(trifluoromethoxy)benzene (37.2 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), $NaHSO_4 \cdot H_2O$ (110.4 mg, 4.0 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound **37** in 59% (32.3 mg) yield as colorless oil. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.83 (d, *J* = 7.8 Hz, 1H), 7.64 (t, *J* = 7.9 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 1H), 6.71 (s, 1H); **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 186.72, 146.73, 134.52, 131.81, 127.46, 127.22, 121.55, 120.52, 69.70; **$^{19}$F NMR (282 MHz, $CDCl_3$)** δ -57.04 (d, *J* = 1.5 Hz); **HRMS (EI)** m/z Calcd for $C_9H_5Cl_2F_3O_2$ 271.9619, Found 189.0161 [M–$^+CHCl_2$]; **IR** (film) 1718, 1604, 1450, 1253, 1203, 1182, 989, 812, 759, 648 $cm^{-1}$.



**38**

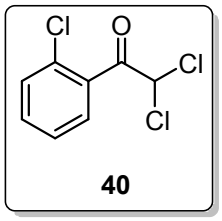
**2,2-dichloro-1-(2-isopropylphenyl)ethan-1-one 38:** Prepared under outlined condition B as in general procedure using 1-ethynyl-2-isopropylbenzene (28.9 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), $NaHSO_4 \cdot H_2O$ (110.4 mg, 4.0 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound **38** in 54% (25.6 mg) yield as colorless oil. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.53 – 7.43 (m, 3H), 7.24 (d, *J* = 5.3 Hz, 1H), 6.54 (s, 1H), 3.30 – 3.12 (m, 1H), 1.24 (d, *J* = 6.8 Hz, 6H); **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 190.05, 149.82, 133.33, 132.42, 127.08, 126.91, 125.51, 69.50, 30.05, 24.18; **HRMS (EI)** m/z Calcd for $C_{11}H_{12}Cl_2O$ 230.0265 Found 194.0493 [M–

HCl]; **IR** (film) 2966, 1716, 1598, 1444, 1265, 1217, 1033, 977, 810, 758, 723, 648, 599 $cm^{-1}$.



**39**

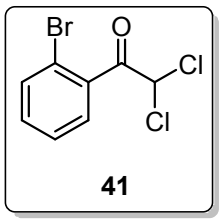
**2,2-dichloro-1-(2-fluorophenyl)ethan-1-one 39:** Prepared under outlined condition B as in general procedure using 1-ethynyl-2-fluorobenzene (24.0 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), $NaHSO_4{\cdot}H_2O$ (110.4 mg, 4.0 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound **39**[9] in 59% (24.6 mg) yield as colorless oil. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.98 (td, *J* = 7.6, 1.8 Hz, 1H), 7.63 (dddd, *J* = 8.3, 7.2, 5.2, 1.8 Hz, 1H), 7.36 – 7.29 (m, 1H), 7.20 (ddd, *J* = 11.4, 8.4, 0.7 Hz, 1H), 6.82 (d, *J* = 2.0 Hz, 1H)； **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 184.39 (d, *J* = 4.1 Hz), 161.16(d, *J* = 255.9 Hz), 136.26 (d, *J* = 9.4 Hz), 132.27 (d, *J* = 2.0 Hz), 125.18 (d, *J* = 3.2 Hz), 121.08 (d, *J* = 12.4 Hz), 116.81 (d, *J* =23.8 Hz), 70.26 (d, *J* = 11.9 Hz)； **$^{19}$F NMR (282 MHz, $CDCl_3$)** δ -108.44 – -108.51 (m)； **MS (EI)** m/z 205; **IR** (film) 2920, 2850, 1710, 1645, 1423, 1365, 1230, 1093, 968, 680, 646 $cm^{-1}$.



**40**

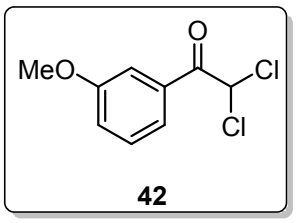
**2,2-dichloro-1-(2-chlorophenyl)ethan-1-one 40:** Prepared under outlined condition B as in general procedure using 1-chloro-2-ethynylbenzene (27.3 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), $NaHSO_4{\cdot}H_2O$ (110.4 mg, 4.0 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound **40**[9] in 62% (27.6 mg) yield as colorless oil. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.61 (d, *J* = 7.7 Hz, 1H), 7.54 – 7.44 (m, 2H), 7.39 (t, *J* = 7.0 Hz, 1H), 6.78 (s, 1H)； **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 188.81, 134.39, 133.12, 131.34, 130.61, 130.58, 127.21, 69.33； **HRMS (ESI)** $[M+Na]^+$ Calcd for $C_8H_5Cl_3ONa$ 244.9298，Found 244.0289; **IR** (film) 1724, 1589,

1469, 1435, 1280, 1207, 1070, 985, 804, 754, 725, 690, 638 $cm^{-1}$.



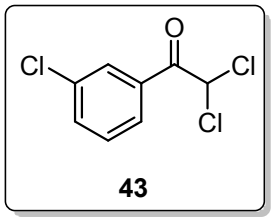
**41**

**1-(2-bromophenyl)-2,2-dichloroethan-1-one 41:** Prepared under outlined condition B as in general procedure using 1-bromo-2-ethynylbenzene (36.2 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), $NaHSO_4 \cdot H_2O$ (110.4 mg, 4.0 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound **41**[9] in 66% (35.3 mg) yield as yellow oil. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.71 – 7.62 (m, 1H), 7.55 (dd, J = 7.4, 1.7 Hz, 1H), 7.36 – 7.46 (m, 2H), 6.73 (s, 1H); **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 189.36, 136.71, 133.66, 132.91, 130.33, 127.60, 119.28, 68.85； **MS (EI)** m/z 266; **IR** (film) 2924, 1726, 1587, 1429, 1288, 1207, 1055, 983, 802, 719, 669, 636 $cm^{-1}$.



**42**

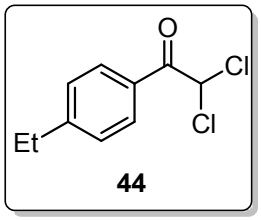
**2,2-dichloro-1-(3-methoxyphenyl)ethan-1-one 42:** Prepared under outlined condition B as in general procedure using 1-ethynyl-3-methoxybenzene (26.4 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), $NaHSO_4 \cdot H_2O$ (110.4 mg, 4.0 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred r under 6 W blue LEDs at room temperature for 24 hours affording compound **42**[10] in 71% (31.5 mg) yield as colorless oil. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.65 (ddd, *J* = 7.7, 1.5, 0.9 Hz, 1H), 7.62 – 7.54 (m, 1H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.19 (ddd, *J* = 8.3, 2.6, 0.8 Hz, 1H), 6.69 (s, 1H), 3.87 (s, 3H)； **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 185.80, 159.99, 132.64, 129.88, 122.05, 121.16, 114.06, 67.73, 55.56； **HRMS (ESI)** $[M+Na]^+$ Calcd for $C_9H_8Cl_2O_2Na$ 240.9794， Found 240.9788; **IR** (film) 1703, 1597, 1581, 1487, 1429, 1282, 1255, 1163, 1045, 877, 808, 736, 682 $cm^{-1}$.



**43**

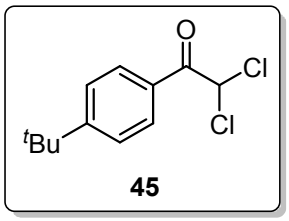
**2,2-dichloro-1-(3-chlorophenyl)ethan-1-one 43:** Prepared

under outlined condition B as in general procedure using 1-chloro-3-ethynylbenzene (27.3 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), $NaHSO_4 \cdot H_2O$ (110.4 mg, 4.0 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound **43**[11] in 62% (27.6 mg) yield as colorless oil. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.06 (t, *J* = 1.9 Hz, 1H), 7.98 (ddd, *J* = 7.9, 1.6, 1.1 Hz, 1H), 7.62 (ddd, *J* = 8.0, 2.1, 1.0 Hz, 1H), 7.47 (t, *J* = 7.9 Hz, 1H), 6.60 (s, 1H)； **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 184.86, 135.30, 134.49, 132.82, 130.18, 129.80, 127.83, 67.68； **MS (EI)** m/z 222; **IR** (film) 1707, 1571, 1471, 1423, 1284, 1220, 1080, 999, 812, 700, 678, 651 $cm^{-1}$.



**44**

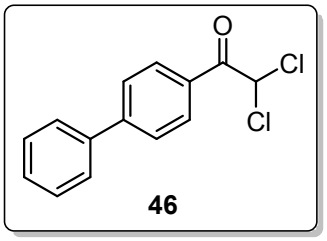
**2,2-dichloro-1-(4-ethylphenyl)ethan-1-one 44:** Prepared under outlined condition B as in general procedure using 1-ethyl-4-ethynylbenzene (26.0 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), $NaHSO_4 \cdot H_2O$ (110.4 mg, 4.0 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound **44**[9] in 55% (23.0 mg) yield as colorless oil. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.06 – 7.98 (m, 2H), 7.35 (t, *J* = 7.4 Hz, 2H), 6.68 (s, 1H) , 2.74 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H)； **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 185.60, 151.95, 129.99, 128.95, 128.47, 67.85, 29.09, 15.00； **MS (EI)** m/z 216; **IR** (film) 2968, 1701, 1604, 1415, 1280, 1224, 1178, 989, 852, 798, 740, 634 $cm^{-1}$.



**45**

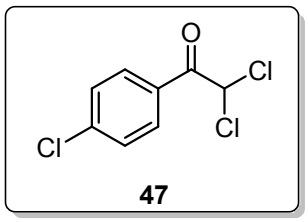
**1-(4-(*tert*-butyl)phenyl)-2,2-dichloroethan-1-one 45:** Prepared under outlined condition B as in general procedure using 1-(*tert*-butyl)-4-ethynylbenzene (31.7 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), $NaHSO_4 \cdot H_2O$ (110.4 mg, 4.0 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the

reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound **45**[12] in 59% (27.2 mg) yield as colorless oil. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.08 – 7.98 (m, 2H), 7.58 – 7.51 (m, 2H), 6.67 (s, 1H), 1.36 (s, 9H)；**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 185.56, 158.73, 129.78, 128.63, 125.95, 67.85, 35.37, 30.98；**MS (EI)** m/z 229; **IR** (film) 2964, 1705, 1604, 1463, 1409, 1365, 1278, 1222, 1109, 989, 854, 792, 702, 628 $cm^{-1}$.



**46**

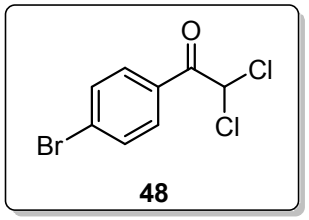
**1-([1,1'-biphenyl]-4-yl)-2,2-dichloroethan-1-one 46** Prepared under outlined condition B as in general procedure using 4-ethynyl-1,1'-biphenyl (35.7 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), $NaHSO_4{\cdot}H_2O$ (110.4 mg, 4.0 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound **46**[9] in 75% (40.2 mg) yield as white solid. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.24 – 8.12 (m, 2H), 7.80 – 7.70 (m, 2H), 7.68 – 7.61 (m, 2H), 7.55 – 7.46 (m, 2H), 7.46 – 7.41 (m, 1H), 6.71 (s, 1H)；**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 185.57, 147.30, 139.37, 130.41, 129.92, 129.10, 128.72, 127.50, 127.34, 67.91；**MS (EI)** m/z 264; **IR** (film) 2920, 1707, 1647, 1423, 1367, 1232, 1093, 904, 729, 669 $cm^{-1}$.



**47**

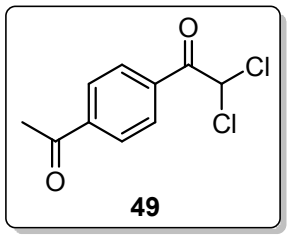
**2,2-dichloro-1-(4-chlorophenyl)ethan-1-one 47:** Prepared under outlined condition B as in general procedure using 1-chloro-4-ethynylbenzene (36.2 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), $NaHSO_4{\cdot}H_2O$ (110.4 mg, 4.0 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound **47**[13] in 63% (28.2 mg) yield as colorless oil. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.10 – 8.02

(m, 2H), 7.54 – 7.46 (m, 2H), 6.59 (s, 1H); **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 184.94, 141.25, 131.24, 129.50, 129.30, 67.78; **MS (EI)** m/z 222; **IR** (film) 2924, 1710, 1589, 1489, 1402, 1274, 1219, 1093, 1014, 848, 788, 713 $cm^{-1}$.



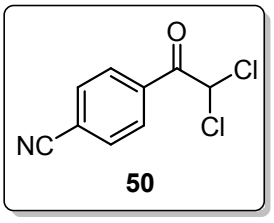
**48**

**1-(4-bromophenyl)-2,2-dichloroethan-1-one 48:** Prepared under outlined condition B as in general procedure using 1-bromo-4-ethynylbenzene (36.2 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), $NaHSO_4 \cdot H_2O$ (110.4 mg, 4.0 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound **48**[13] in 63% (34.7 mg) yield as colorless oil. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.02 – 7.92 (m, 2H), 7.71 – 7.64 (m, 2H), 6.58 (s, 1H); **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 185.17, 132.30, 131.26, 129.30, 67.75; **MS (EI)** m/z 268; **IR** (film) 1705, 1583, 1487, 1398, 1273, 1217, 1072, 1010, 987, 844, 783, 619, 588 $cm^{-1}$.



**49**

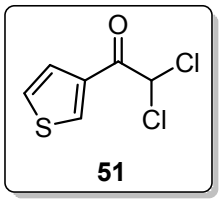
**1-(4-acetylphenyl)-2,2-dichloroethan-1-one 49:** Prepared under outlined condition B as in general procedure using 1-(4-ethynylphenyl)ethan-1-one (28.2 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), $NaHSO_4 \cdot H_2O$ (110.4 mg, 4.0 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound **49**[13] in 53% (25.0 mg) yield as white solid. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.18 (d, $J$ = 8.3 Hz, 2H), 8.07 (d, $J$ = 8.2 Hz, 2H), 6.65 (s, 1H), 2.66 (s, 3H); **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 197.10, 185.46, 141.08, 134.52, 130.08, 128.56, 67.83, 26.92; **MS (EI)** m/z 230; **IR** (film) 1699, 1680, 1504, 1402, 1265, 1226, 962, 862, 790, 715, 651 $cm^{-1}$.



**50**

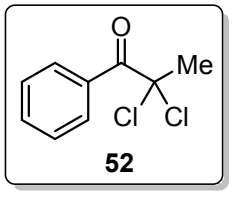
**4-(2,2-dichloroacetyl)benzonitrile 50:** Prepared under

outlined condition B as in general procedure using 4-ethynylbenzonitrile (25.4 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), $NaHSO_4 \cdot H_2O$ (110.4 mg, 4.0 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound **50**[11] in 63% (26.9 mg) yield as white solid. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.25 – 8.19 (m, 2H), 7.85 – 7.80 (m, 2H), 6.57 (s, 1H)；**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 184.83, 134.35, 132.58, 130.32, 117.69, 117.48, 67.72；**HRMS (ESI)** $[M-H]^+$ Calcd for $C_9H_4Cl_2NO$ 211.9670，Found 211.9644; **IR** (film) 2922, 2233, 1712, 1606, 1406, 1282, 1220, 993, 858, 802, 732, 626 $cm^{-1}$.



**51**

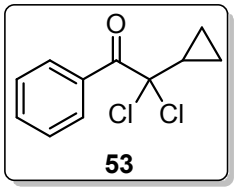
**2,2-dichloro-1-(thiophen-3-yl)ethan-1-one 51:** Prepared under outlined condition B as in general procedure using 3-ethynylthiophene (21.6 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), $NaHSO_4 \cdot H_2O$ (110.4 mg, 4.0 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound **51**[13] in 45% (16.9 mg) yield as pale yellow oil. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.38 (dd, $J$ = 2.9, 1.2 Hz, 1H), 7.68 (dd, $J$ = 5.1, 1.2 Hz, 1H), 7.39 (dd, $J$ = 5.1, 2.9 Hz, 1H), 6.42 (s, 1H)；**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 180.36, 135.50, 134.97, 127.96, 126.73, 68.63；**MS (EI)** m/z 194; **IR** (film) 3109, 1693, 1508, 1411, 1280, 1224, 881, 821, 721, 680, 651 $cm^{-1}$.



**52**

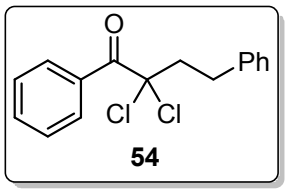
**2,2-dichloro-1-phenylpropan-1-one 52:** Prepared under outlined condition B as in general procedure using prop-1-yn-1-ylbenzene (23.2 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), $NaHSO_4 \cdot H_2O$ (110.4 mg, 4.0 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound **52**[8] in 62% (25.0 mg) yield as

colorless oil. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.41 – 8.23 (m, 2H), 7.64 – 7.55 (m, 1H), 7.47 (dd, *J* = 10.8, 4.8 Hz, 2H), 2.36 (s, 3H)； **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 188.12, 133.61, 131.31, 131.19, 128.13, 82.74, 34.30； **MS (EI)** m/z 202; **IR** (film) 1689, 1597, 1448, 1379, 1255, 1074, 960, 808, 686, 640 $cm^{-1}$.



**53**

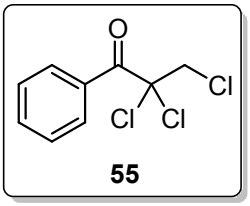
**2,2-dichloro-2-cyclopropyl-1-phenylethan-1-one 53:** Prepared under outlined condition B as in general procedure using (cyclopropylethynyl)benzene (28.4 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), $NaHSO_4{\cdot}H_2O$ (110.4 mg, 4.0 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound **53** in 52% (24.3 mg) yield as colorless oil. **$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.29 (dt, *J* = 8.6, 1.5 Hz, 2H), 7.63 – 7.54 (m, 1H), 7.51 – 7.43 (m, 2H), 2.01 (tt, *J* = 8.1, 5.3 Hz, 1H), 0.94 – 0.82 (m, 4H)； **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 188.31, 133.33, 132.23, 130.95, 128.09, 89.95, 23.04, 4.66； **HRMS (EI)** m/z Calcd for $C_{11}H_{10}Cl_2O$ 228.0109 Found 193.0418 [M–Cl]; **IR** (film) 2920, 2848, 1716, 1633, 1365, 1230, 1093, 1024, 954, 690, 569 $cm^{-1}$.



**54**

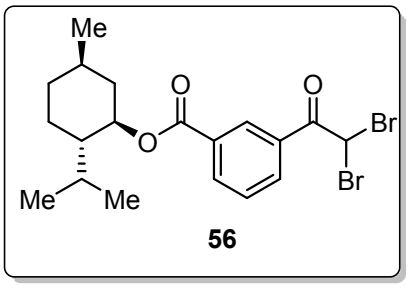
**2,2-dichloro-1,4-diphenylbutan-1-one 54:** Prepared under outlined condition B as in general procedure using but-1-yne-1,4-diyldibenzene (41.2 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), $NaHSO_4{\cdot}H_2O$ (110.4 mg, 4.0 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound **54** in 48% (25.0 mg) yield as colorless oil. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.42 – 8.20 (m, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.39 – 7.19 (m, 5H), 3.14 – 2.98 (m, 2H), 2.91 – 2.72 (m, 2H)； **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 188.20, 140.30, 133.54, 131.94, 131.00, 128.61, 128.15, 126.33, 86.69, 46.42, 31.29； **HRMS (EI)** Calcd for $C_{16}H_{14}Cl_2O$ 292.0422, Found 292.0420; **IR** (film)

2935, 1716, 1691, 1597, 1448, 1363, 1249, 1224, 821, 688 $cm^{-1}$.



**55**

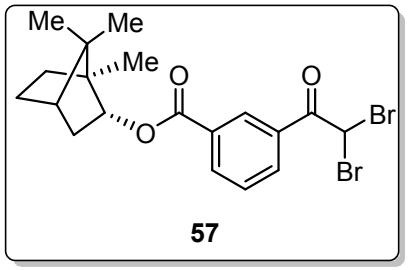
**2,2,3-trichloro-1-phenylpropan-1-one 55:** Prepared under outlined condition B as in general procedure using (3-chloroprop-1-yn-1-yl)benzene (30.1 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), $NaHSO_4{\cdot}H_2O$ (110.4 mg, 4.0 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound **55** in 63% (30.0 mg) yield as colorless oil. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.26 (dt, *J* = 8.6, 1.6 Hz, 2H), 7.67 – 7.59 (m, 1H), 7.54 – 7.46 (m, 2H), 4.33 (s, 2H)； **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 186.89, 134.00, 131.39, 130.84, 128.30, 83.41, 52.27； **HRMS (EI)** m/z Calcd for $C_9H_7Cl_3O$ 235.9562 Found 200.9874 [M–Cl]; **IR** (film) 1689, 1597, 1448, 1413, 1259, 1186, 937, 840, 804, 686, 651, 557 $cm^{-1}$.



**56**

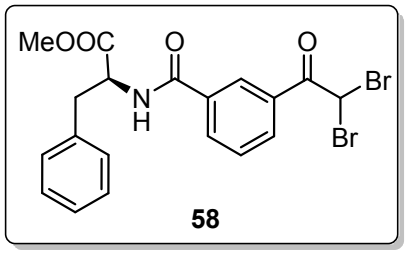
**(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 3-(2,2-dibromoacetyl)benzoate 56:** Prepared under outlined condition A as in general procedure using (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 3-ethynylbenzoate (56.9 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), $NaHSO_4{\cdot}H_2O$ (96.7 mg, 3.5 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound **56** in 83% (76.4 mg) yield as colorless oil. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.72 (s, 1H), 8.33 – 8.24 (m, 2H), 7.60 (t, *J* = 7.8 Hz, 1H), 6.71 (s, 1H), 4.97 (td, *J* = 10.9, 4.3 Hz, 1H), 2.13 (d, *J* = 11.9 Hz, 1H), 1.94 (dt, *J* = 13.8, 6.9 Hz, 1H), 1.74 (d, *J* = 11.1 Hz, 2H), 1.57 (d, *J* = 11.1 Hz, 2H), 1.19 – 1.08 (m, 2H), 0.93 (t, *J* = 5.8 Hz, 7H), 0.80 (d, *J* = 6.9 Hz, 3H)； **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 185.33, 164.78, 135.07, 133.62, 131.80, 131.13, 130.71, 129.15,

75.75, 47.22, 40.91, 39.34, 34.25, 31.47, 26.60, 23.67, 22.02, 20.75, 16.58；**HRMS (ESI)** $[M+Na]^+$ Calcd for $C_{19}H_{24}Br_2O_3Na$ 480.9990, Found 480.9998; **IR** (film) 2954, 1705, 1602, 1456, 1298, 1242, 1188, 1099, 960, 779, 723, 675, 630 $cm^{-1}$.



**57**

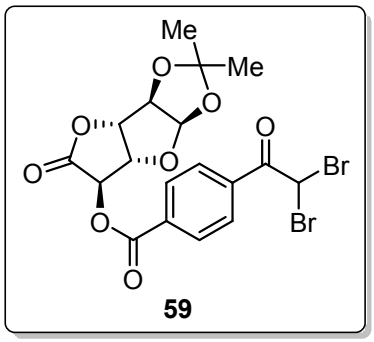
**(1*S*,2*S*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 3-(2,2-dibromoacetyl)benzoate 57:** Prepared under outlined condition A as in general procedure using (1*S*,2*S*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 3-ethynylbenzoate (56.5 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), $NaHSO_4{\cdot}H_2O$ (96.7 mg, 3.5 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound **57** in 77% (70.4 mg) yield as colorless syrup. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.79 (t, *J* = 1.6 Hz, 1H), 8.30 (tt, *J* = 7.7, 1.3 Hz, 2H), 7.62 (t, *J* = 7.8 Hz, 1H), 6.67 (s, 1H), 5.15 (ddd, *J* = 9.9, 3.3, 2.3 Hz, 1H), 2.55 – 2.44 (m, 1H), 2.18 – 2.08 (m, 1H), 1.90 – 1.73 (m, 2H), 1.51 – 1.39 (m, 1H), 1.33 (ddd, *J* = 12.4, 9.5, 4.4 Hz, 1H), 1.14 (dd, *J* = 13.8, 3.4 Hz, 1H), 0.95 (d, *J* = 19.4 Hz, 9H)；**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 185.30, 165.49, 134.98, 133.71, 131.73, 131.09, 130.82, 129.22, 81.40, 49.19, 47.97, 44.99, 39.30, 36.91, 28.10, 27.43, 19.73, 18.93, 13.65；**HRMS (ESI)** $[M+Na]^+$ Calcd for $C_{19}H_{22}Br_2O_3Na$ 478.9833，Found 478.9823; **IR** (film) 2953, 1705, 1602, 1307, 1244, 1190, 1116, 977, 779, 675, 628 $cm^{-1}$.



**58**

**methyl (3-(2,2-dibromoacetyl)benzoyl)-*L*-phenylalaninate 58:** Prepared under outlined condition A as in general procedure using methyl (3-ethynylbenzoyl)-*L*-phenylalaninate (61.4 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), $NaHSO_4{\cdot}H_2O$ (96.7 mg, 3.5 equiv.),

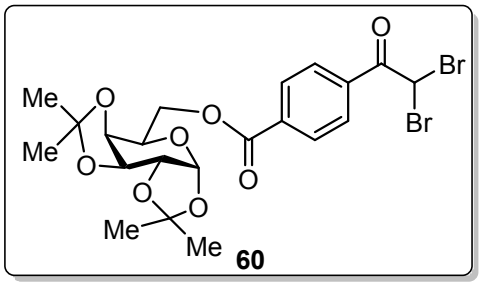
$H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound **58** in 67% (64.7 mg) yield as white solid. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.37 (t, *J* = 1.7 Hz, 1H), 8.26 – 8.16 (m, 1H), 7.98 – 7.90 (m, 1H), 7.55 (td, *J* = 7.8, 2.7 Hz, 1H), 7.33 – 7.23 (m, 3H), 7.17 – 7.11 (m, 2H), 6.76 – 6.56 (m, 2H), 5.08 (dt, *J* = 7.6, 5.8 Hz, 1H), 3.78 (s, 3H), 3.26 (qd, *J* = 13.9, 5.8 Hz, 2H)； **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 185.26, 171.94, 165.47, 135.66, 134.79, 132.73, 132.65, 131.24, 129.40, 129.30, 128.79, 128.18, 127.39, 53.68, 52.61, 39.33, 37.83； **HRMS (ESI)** $[M+H]^+$ Calcd for $C_{19}H_{17}Br_2NO_4Na$ 503.9422，Found 503.9423; **IR** (film) 1739, 1701, 1647, 1535, 1435, 1261, 1203, 995, 702, 632 $cm^{-1}$.



**59**

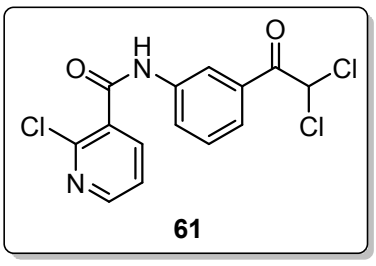
**(3a*R*,3b*S*,6*R*,6a*S*,7a*R*)-2,2-dimethyl-5-oxohexahydrofuro[2',3':4,5]furo[2,3-d][1,3]dioxol-6-yl 4-(2,2-dibromoacetyl)benzoate 59:** Prepared under outlined condition A as in general procedure using (3a*R*,3b*S*,6*R*,6a*S*,7a*R*)-2,2-dimethyl-5-oxohexahydrofuro[2',3':4,5]furo[2,3-d][1,3]dioxol-6-yl 4-ethynylbenzoate (78.8 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), $NaHSO_4 \cdot H_2O$ (96.7 mg, 3.5 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound **59** in 59% (61.6 mg) yield as white solid. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.26 – 8.08 (m, 4H), 6.65 (s, 1H), 6.02 (d, *J* = 3.5 Hz, 1H), 5.33 – 5.09 (m, 2H), 4.94 (d, *J* = 3.6 Hz, 1H), 4.90 (d, *J* = 3.5 Hz, 1H), 1.49 (s, 3H), 1.36 (s, 3H)； **$^{13}$C NMR (101 MHz, $CDCl_3$)**

δ 185.24, 170.34, 164.06, 135.26, 132.48, 130.51, 129.91, 113.33, 106.23, 85.47, 82.16, 81.42, 73.62, 39.16, 27.15, 26.60；**HRMS (ESI)** $[M+Na]^+$ Calcd for $C_{18}H16Br_2O_8Na$ 540.9110，Found 540.9105; **IR** (film) 2922, 2850, 1797, 1730, 1705, 1261, 1180, 1105, 1074, 1024, 867, 736, 682, 563 $cm^{-1}$.



**60**

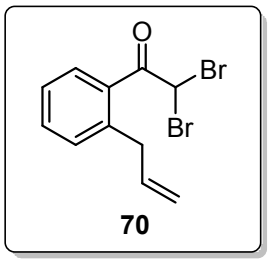
**((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 4-(2,2-dibromoacetyl)benzoate 60:** Prepared under outlined condition A as in general procedure using ((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 4-ethynylbenzoate (77.6 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), $NaHSO_4{\cdot}H_2O$ (96.7 mg, 3.5 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound **60** in 72% (81.1 mg) yield as white solid. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.23 – 8.05 (m, 4H), 6.66 (s, 1H), 5.56 (d, *J* = 5.0 Hz, 1H), 4.65 (dd, *J* = 7.9, 2.5 Hz, 1H), 4.51 (ddd, *J* = 19.3, 11.6, 6.2 Hz, 2H), 4.33 (ddd, *J* = 9.7, 6.4, 2.2 Hz, 2H), 4.22 – 4.14 (m, 1H), 1.51 (s, 3H), 1.47 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H)；**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 185.46, 165.18, 134.93, 134.29, 130.08, 129.70, 109.81, 108.85, 96.34, 71.12, 70.77, 70.49, 66.08, 64.59, 39.35, 26.04, 25.98, 24.96, 24.51；**HRMS (ESI)** $[M+Na]^+$ Calcd for $C_{21}H_{24}Br_2O_8Na$ 584.9736，Found 584.9707; **IR** (film) 2987, 1722, 1705, 1382, 1263, 1211, 1103, 1068, 1004, 896, 869, 734, 655 $cm^{-1}$.



**61**

**2-chloro-*N*-(3-(2,2-dichloroacetyl)phenyl)nicotinamide 61:** Prepared under outlined condition B as in general procedure

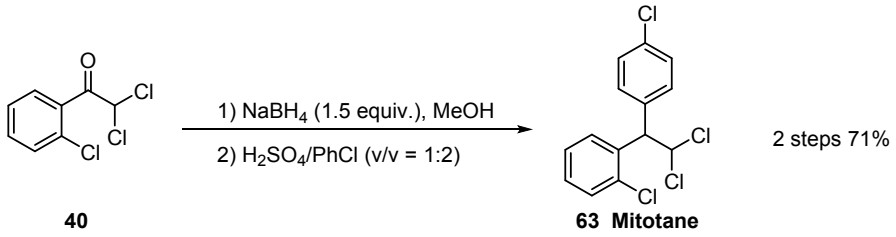
using 2-chloro-*N*-(3-ethynylphenyl)nicotinamide (51.3 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), $NaHSO_4 \cdot H_2O$ (110.4 mg, 4.0 equiv.), $H_2O$ (108.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound **61** in 80% (54.9 mg) yield as colorless syrup. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.65 (s, 1H), 8.48 (d, *J* = 3.9 Hz, 1H), 8.31 (s, 1H), 8.14 (d, *J* = 7.0 Hz, 1H), 8.03 (d, *J* = 7.9 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 1H), 7.38 (dd, *J* = 7.4, 4.8 Hz, 1H), 6.70 (s, 1H)； **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 185.59, 163.17, 151.51, 147.02, 139.81, 138.12, 132.24, 131.09, 129.86, 129.26, 126.20, 122.99, 121.09, 67.70； **HRMS (ESI)** $[M+Na]^+$ Calcd for $C_{14}H_9Cl_3N_2O_2Na$ 364.9627, Found 364.0628; **IR** (film) 1664, 1579, 1548, 1487, 1435, 1400, 1319, 1139, 1066, 813, 756, 682, 659 $cm^{-1}$.



**70**

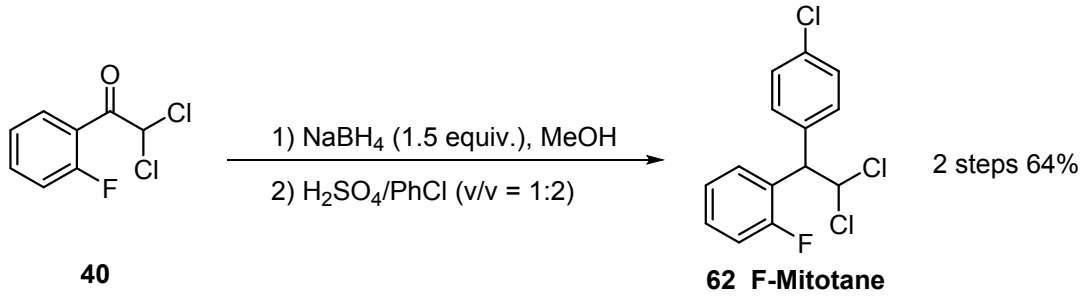
**1-(2-allylphenyl)-2,2-dibromoethan-1-one 70:** Prepared under outlined condition A as in general procedure using 1-allyl-2-ethynylbenzene (14.2 mg, 0.1 mmol, 1.0 equiv.), NaBr (25.7 mg, 2.5 equiv.), $NaHSO_4 \cdot H_2O$ (43.8 mg, 3.5 equiv.), $H_2O$ (54.0 mg, 30.0 equiv.) were dissolved in $CH_3CN$ (1.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound **70** in 30% (9.5 mg) yield as colorless oil. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.67 (d, *J* = 7.8 Hz, 1H), 7.49 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.37 – 7.29 (m, 2H), 6.64 (s, 1H), 6.03 – 5.94 (m, 1H), 5.10 – 5.00 (m, 2H), 3.58 (d, *J* = 6.5 Hz, 2H)； **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 188.96, 141.52, 136.60, 132.75, 132.52, 131.57, 128.15, 128.24, 116.58, 42.15, 37.89； **HRMS (EI)** m/z Calcd for $C_{11}H_{10}Br_2O$ 315.9098, Found 315.9095; **IR** (film) 2924, 2850, 1712, 1571,1436, 1363, 1255, 1220, 974, 920, 794, 634 $cm^{-1}$.

### 3) Procedure for Synthesis of Mitotane and analog



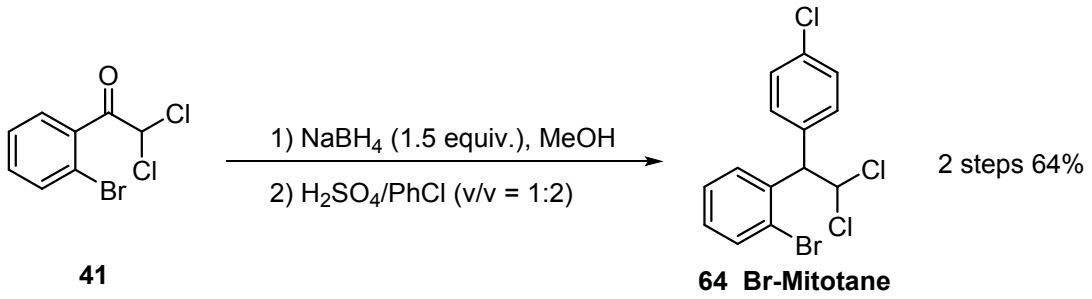

**40** **63 Mitotane**

In schlenk tube, 2, 2-dichloro-1-(2-chlorophenyl)ethan-1-one **40** (150.0 mg, 0.67 mmol) was dissolved in methanol (3.0 mL) and evacuated and refilled with nitrogen (three cycles). The reaction mixture was stirred in ice path for 10 min, then $NaBH_4$ (12.7 mg, 0.5 equiv.) was added into the mixture. The reaction mixture was quenched by 1N HCl aqueous after stirred at room temperature for 20 min. The mixture was purified by column chromatography on silica gel to give colorless oil in 80% yield (95.6 mg). Subsequently, the product (12.4 mg, 0.055 mmol) was dissolved in chlorobenzene (0.5 mL) and concentrated $H_2SO_4$ (0.25 mL) was added dropwise into the mixture and stirred at room temperature for 10 min, then quenched by saturated $NaHCO_3$ aqueous and extracted with DCM (5 mL*3). The organic layer was purified by column chromatography on silica gel to give **Mitotane 63** colorless syrup in 89% yield (15.0 mg). **$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.48 – 7.18 (m, 9H), 6.37 (d, $J$ = 8.7 Hz, 1H), 5.20 (d, $J$ = 8.7 Hz, 1H)； **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 137.22, 136.79, 134.25, 133.66, 130.30, 128.84, 128.82, 128.44, 127.16, 73.79, 57.23； **HRMS (EI)** m/z Calcd for $C_{14}H_{10}Cl_4$ 317.9537, Found 317.9542; **IR** (film) 1490, 1422, 1409, 1093, 1037, 1014, 879, 771, 750, 734, 686, 609 $cm^{-1}$.




**40** **62 F-Mitotane**

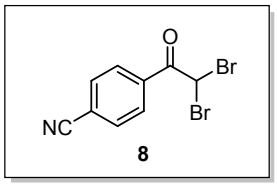
In schlenk tube, 2,2-dichloro-1-(2-fluorophenyl)ethan-1-one (30.0 mg, 0.14 mmol) was dissolved in methanol (1.0 mL) and evacuated and refilled with nitrogen (three cycles). The reaction mixture was stirred in ice path for 10 min, then $NaBH_4$ (2.6 mg, 0.5 equiv.) was added into the mixture. The reaction mixture was quenched by 1N HCl aqueous after stirred at room temperature for 20 min. The mixture was purified by column chromatography on silica gel to give colorless oil in 72% yield (21.8 mg). Subsequently, the product (21.8 mg, 0.1 mmol) was dissolved in chlorobenzene (0.5 mL) and $H_2SO_4$ (0.25 mL) was added dropwise into the mixture and stirred at room temperature for 10 min, then quenched by saturated $NaHCO_3$ aqueous and extracted with DCM (5 mL*3). The organic layer was purified by column chromatography on silica gel to give **F-Mitotane 62** colorless syrup in 90% yield (27.0 mg). **$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.38 – 7.23 (m, 6H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.09 – 7.03 (m, 1H), 6.45 (d, *J* = 9.2 Hz, 1H), 4.82 (d, *J* = 9.2 Hz, 1H)； **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 160.23 (d, *J* = 247.17), 137.30, 133.66, 129.87 (d, *J* = 1.4 Hz), 129.46 (d, *J* = 8.6 Hz), 129.33 (d, *J* = 4.0 Hz), 128.94, 127.02 (d, *J* = 13.8 Hz), 124.51 (d, *J* = 3.5 Hz), 116.12 (d, *J* = 22.7 Hz), 73.45, 56.57; **HRMS (EI)** m/z Calcd for $C_{14}H_{10}Cl_3F$ 301.9832, Found 301.9835; **IR** (film) 2926, 1712, 1490, 1365, 1232, 1093, 1014, 823, 761, 750, 607 $cm^{-1}$.

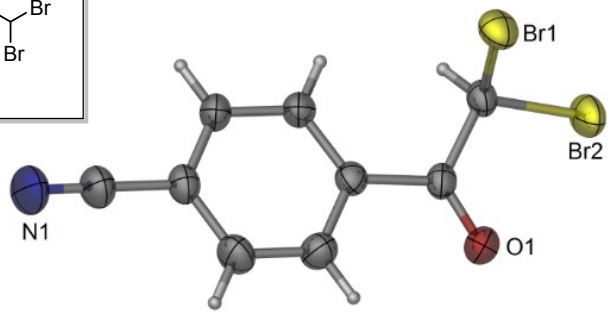



**41** **64 Br-Mitotane**

In schlenk tube, 1-(2-bromophenyl)-2,2-dichloroethan-1-one (90.0 mg, 0.336 mmol) was dissolved in methanol (1.0 mL) and evacuated and refilled with nitrogen (three cycles). The reaction mixture was stirred in ice path for 10 min, then $NaBH_4$ (6.3 mg, 0.5 equiv.) was added into the mixture. The reaction mixture was quenched by 1N HCl aqueous after stirred at room temperature for 20 min. The mixture was purified by column chromatography on silica gel to give colorless oil in 72% yield (65.0 mg). Then **3l'** (15.0 mg, 0.055 mmol) was dissolved in chlorobenzene (0.5 mL) and $H_2SO_4$ (0.25 mL) was added dropwise into the mixture and stirred at room temperature for 10 min, then quenched by saturated $NaHCO_3$ aqueous and extracted with DCM (5 mL*3). The organic layer was purified by column chromatography on silica gel to give **Br-Mitotane 64** colorless syrup in 90% yield (18.1 mg). **$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.59 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.43 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.37 – 7.29 (m, 5H), 7.15 (td, *J* = 7.8, 1.6 Hz, 1H), 6.36 (d, *J* = 8.6 Hz, 1H), 5.21 (d, *J* = 8.6 Hz, 1H)； **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 138.81, 136.74, 133.66, 133.63, 130.34, 129.13, 128.81, 128.60, 73.90, 59.60； **HRMS (EI)** m/z Calcd for $C_{14}H_{10}BrCl_3$ 361.9031, Found 361.9037; **IR** (film) 2922, 2852, 1490, 1469, 1438, 1409, 1095, 1014, 769, 748, 705, 663, 609 $cm^{-1}$

# V. X-ray Crystallography Analysis of Compound 8



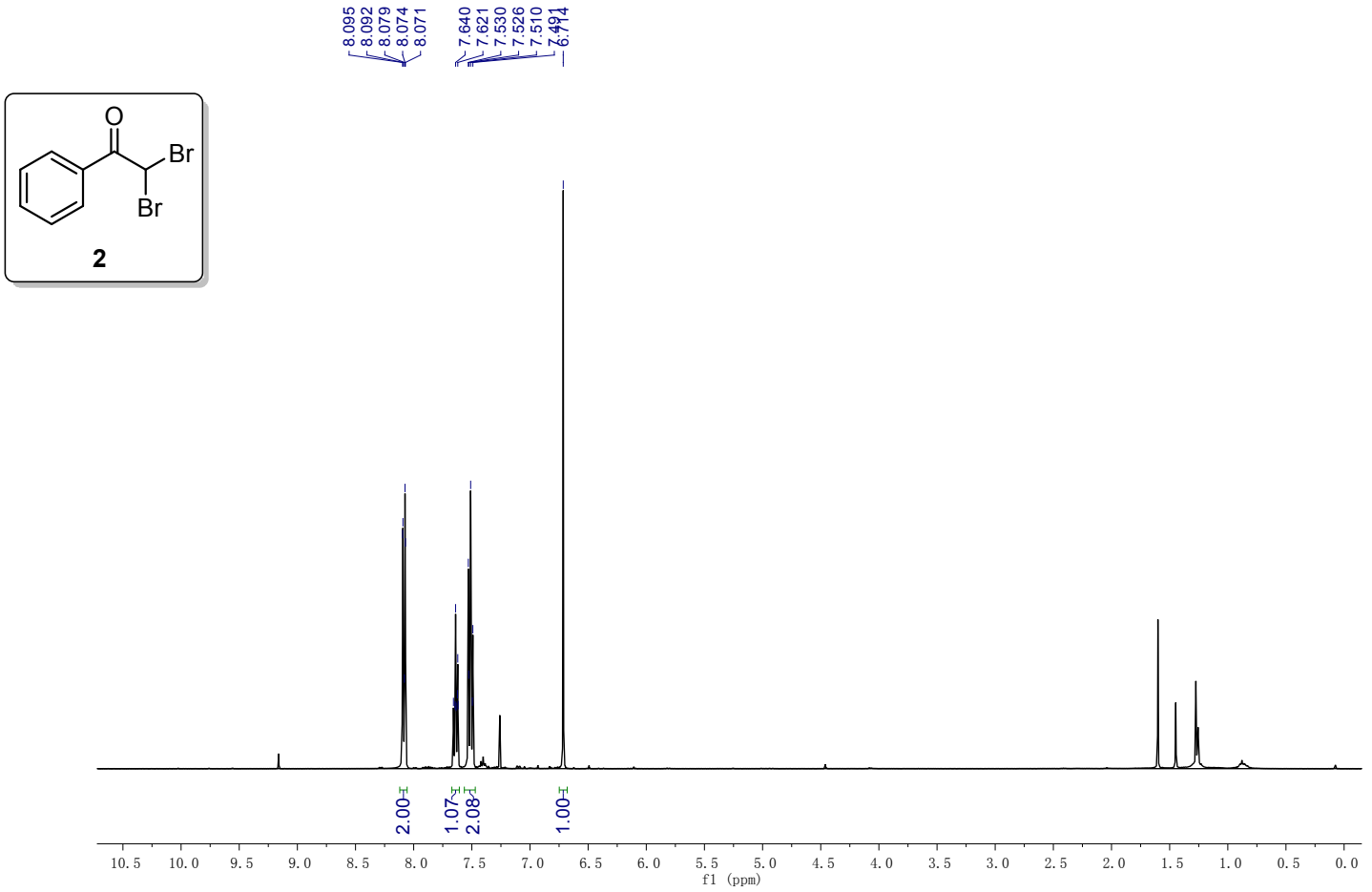




**CCDC 1915404**

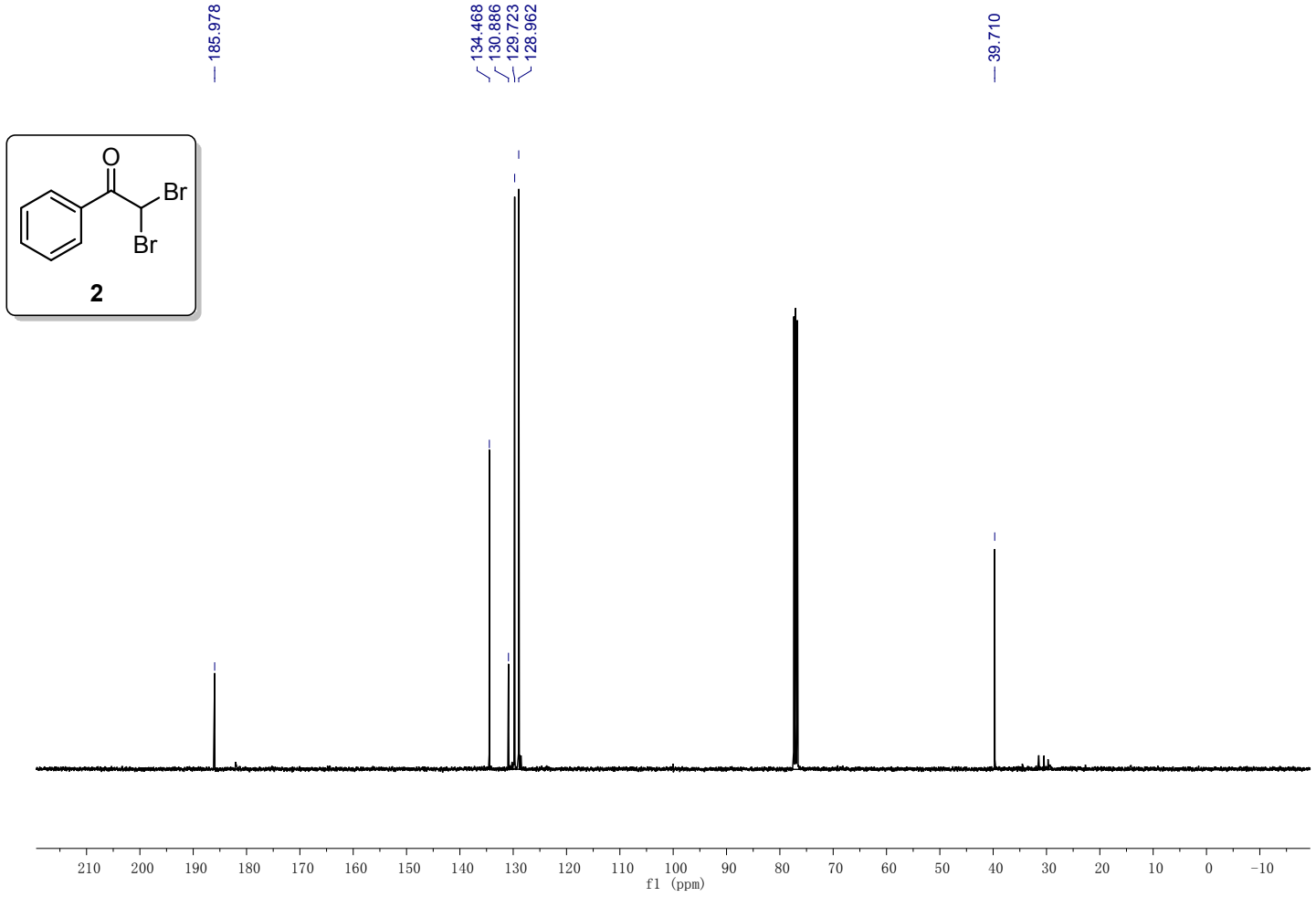
| | |
|---|---|
| Empirical formula | $C_9H_5Br_2NO$ |
| Formula weight | 302.96 |
| Temperature/K | 293 (2) |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| a/Å | 8.40930 (10) |
| b/Å | 9.09290 (10) |
| c/Å | 13.3012 (2) |
| *α*/° | 90 |
| *β*/° | 104.1410 (10) |
| *γ*/° | 90 |
| Volume/Å$^3$ | 986.26 (2) |
| Z | 4 |
| *ρ*calcg/cm$^3$ | 2.040 |
| μ/mm$^{-1}$ | 10.094 |
| F (000) | 576.0 |
| Crystal size/mm$^3$ | 0.46 × 0.45 × 0.42 |
| Radiation | CuK*α* (λ = 1.54184) |
| 2Θ range for data collection/° | 11.332 to 134.058 |
| Index ranges | -9 ≤ h ≤ 10, -10 ≤ k ≤ 10, -15 ≤ l ≤ 15 |
| Reflections collected | 19779 |
| Independent reflections | 1733 [$R_{int}$ = 0.1818, $R_{sigma}$ = 0.0614] |
| Data/restraints/parameters | 1733/0/119 |
| Goodness-of-fit on $F^2$ | 1.066 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0487, w$R_2$ = 0.1264 |
| Final R indexes [all data] | $R_1$ = 0.0497, w$R_2$ = 0.1280 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.79/-1.43 |

# VI. NMR Spectra

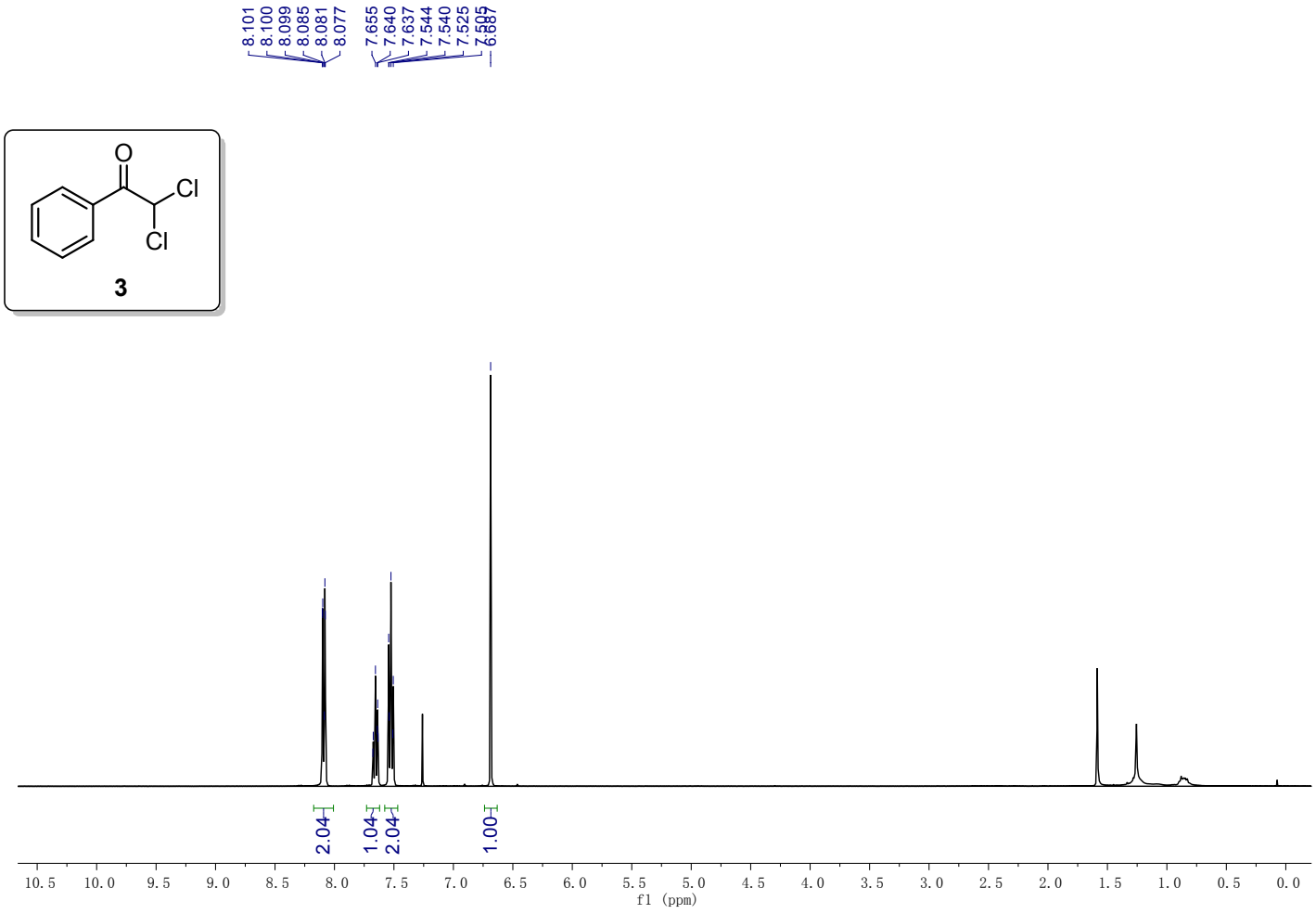
**$^1$H NMR of 2**



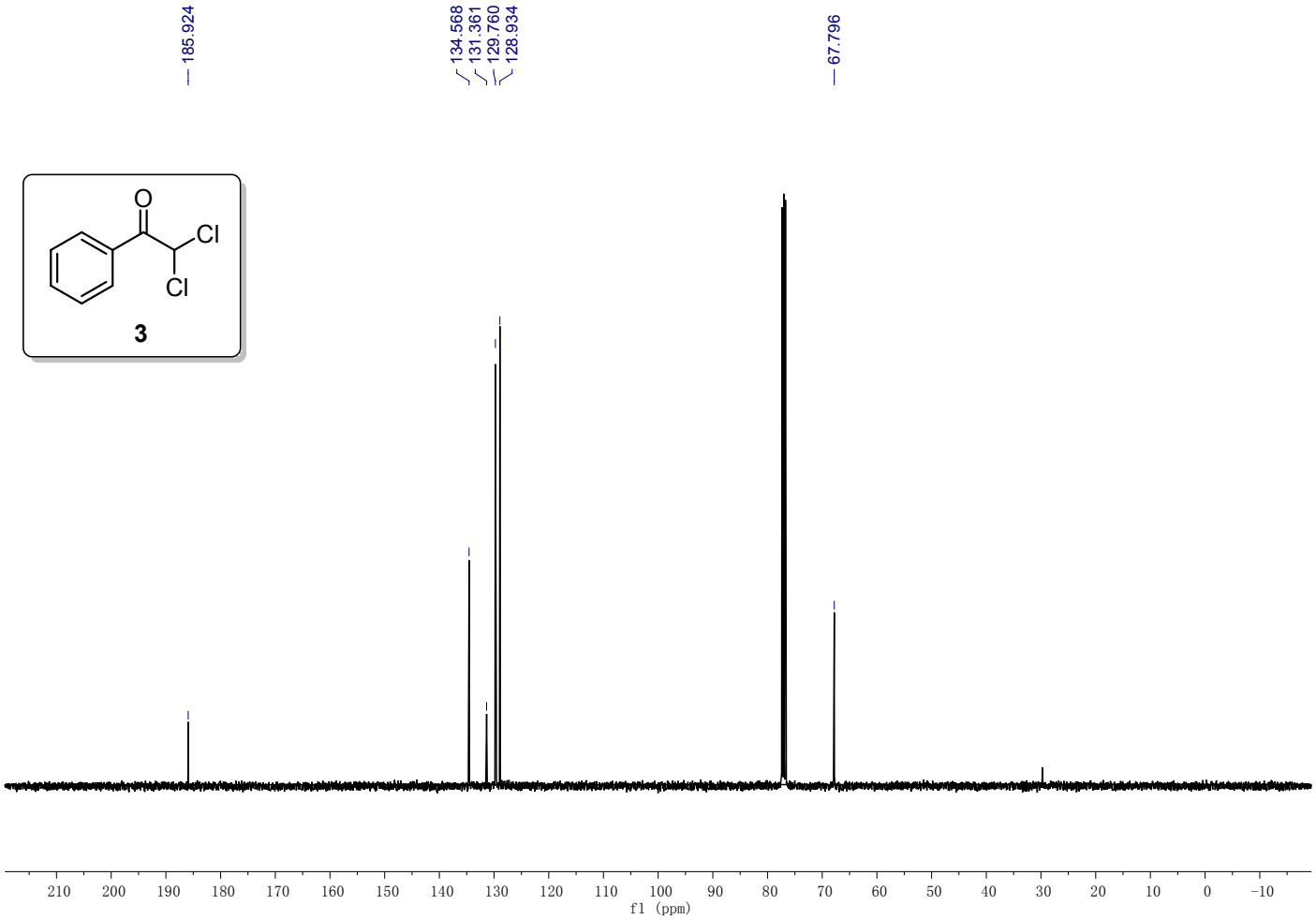
## $^{13}$C NMR of 2


185.978
134.468
130.886
129.723
128.962
39.710
O
Br
Br
2
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)

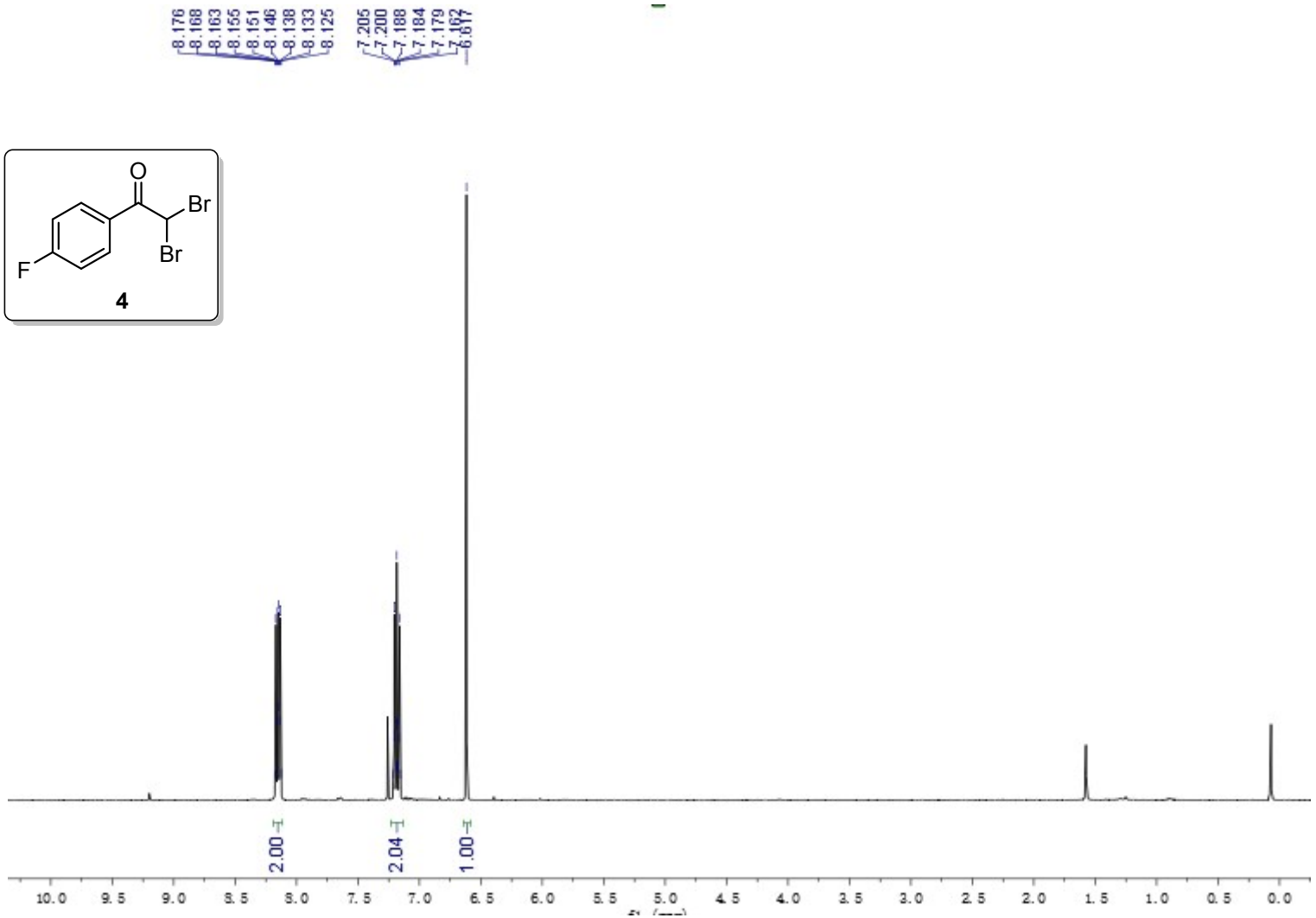
## $^1$H NMR of 3


8.101
8.100
8.099
8.085
8.081
8.077
7.655
7.640
7.637
7.544
7.540
7.525
7.505
7.497
6.887
O
Cl
Cl
3
2.04
1.04
2.04
1.00
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
f1 (ppm)

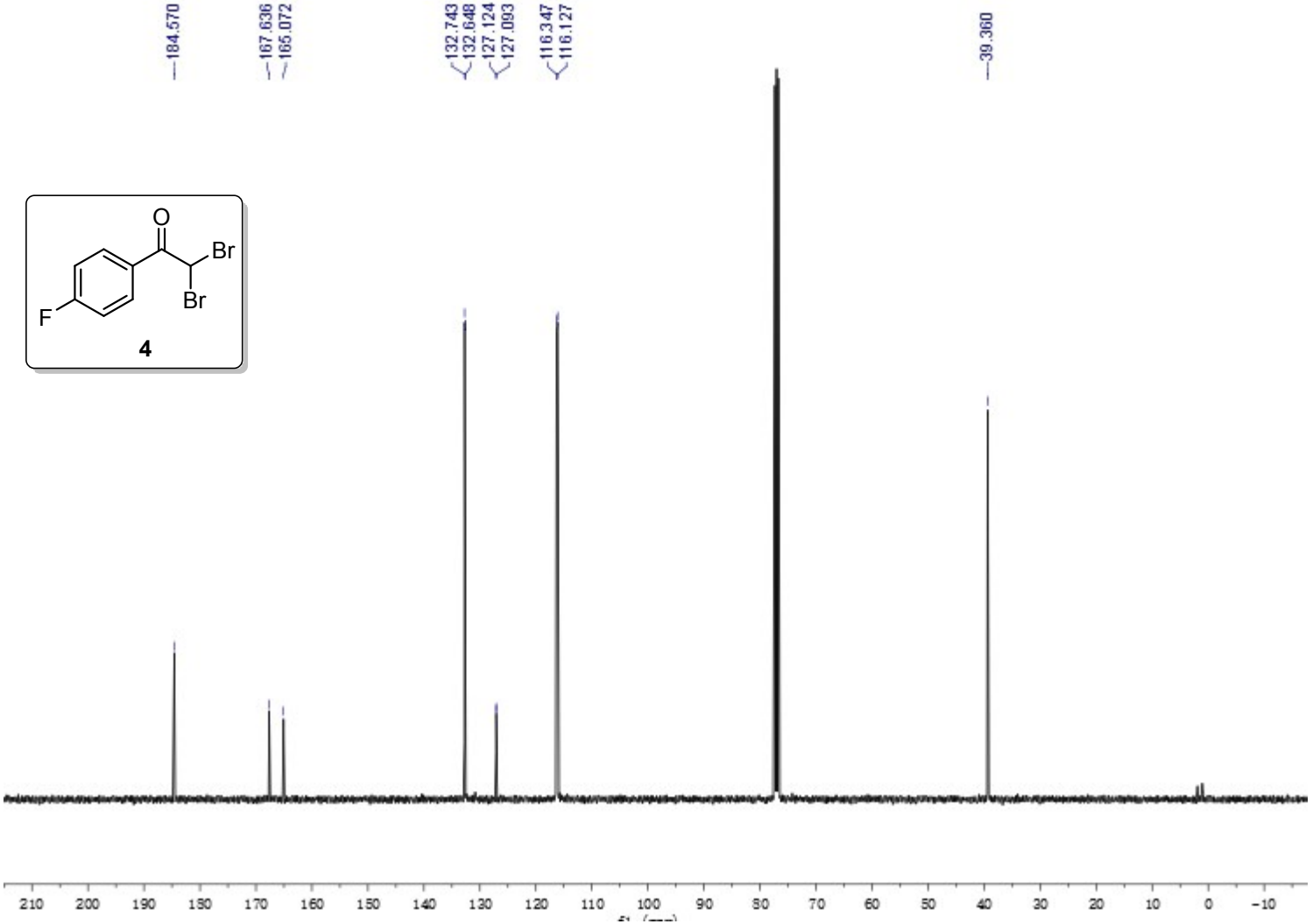
## $^{13}$C NMR of 3


185.924
134.568
131.361
129.760
128.934
67.796
O
Cl
Cl
3
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)

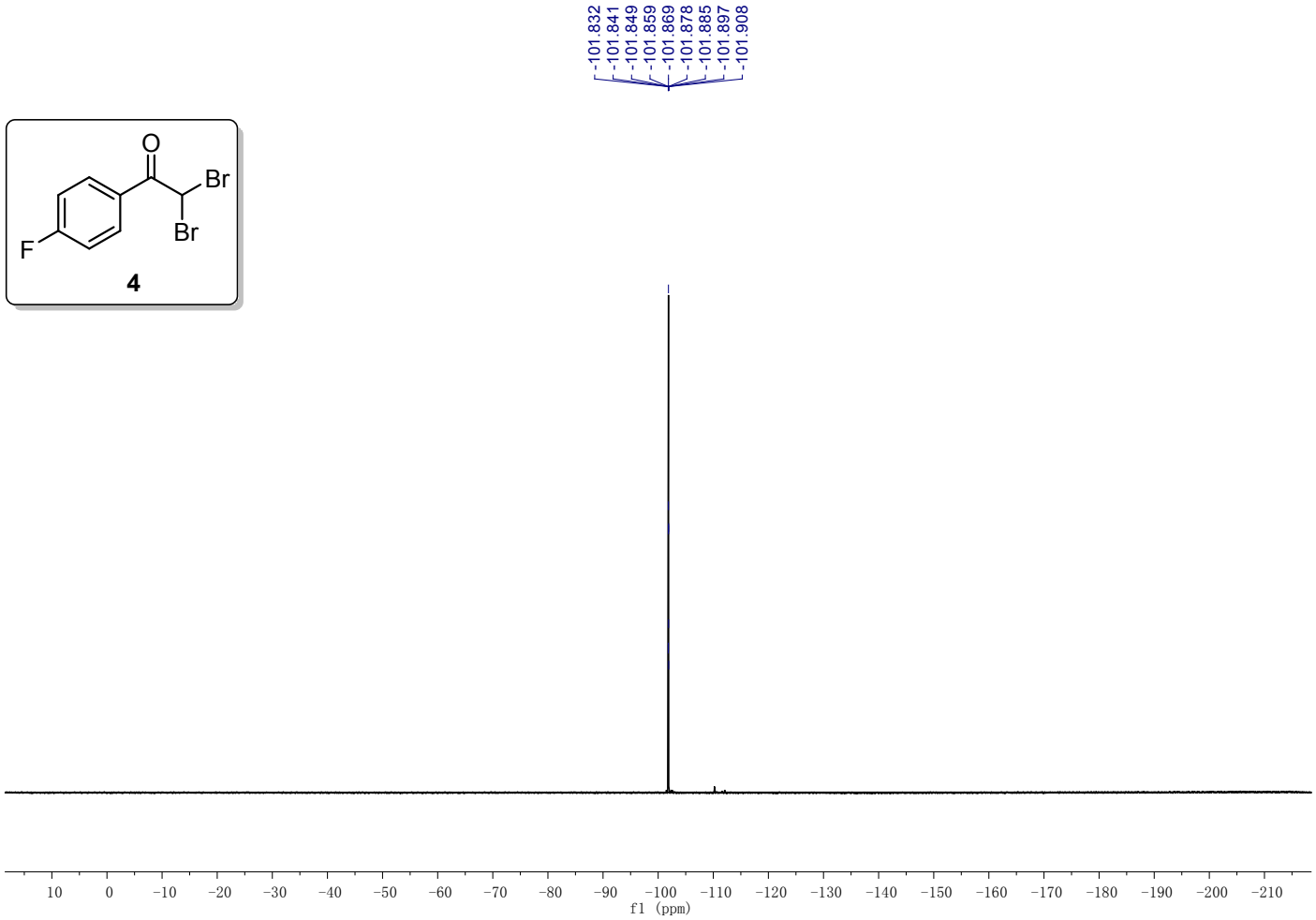
**$^1$H NMR of 4**


8.176
8.168
8.163
8.155
8.151
8.146
8.138
8.133
8.125
7.205
7.200
7.188
7.184
7.179
7.162
7.157
6.617
O
Br
Br
F
4
2.00
2.04
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

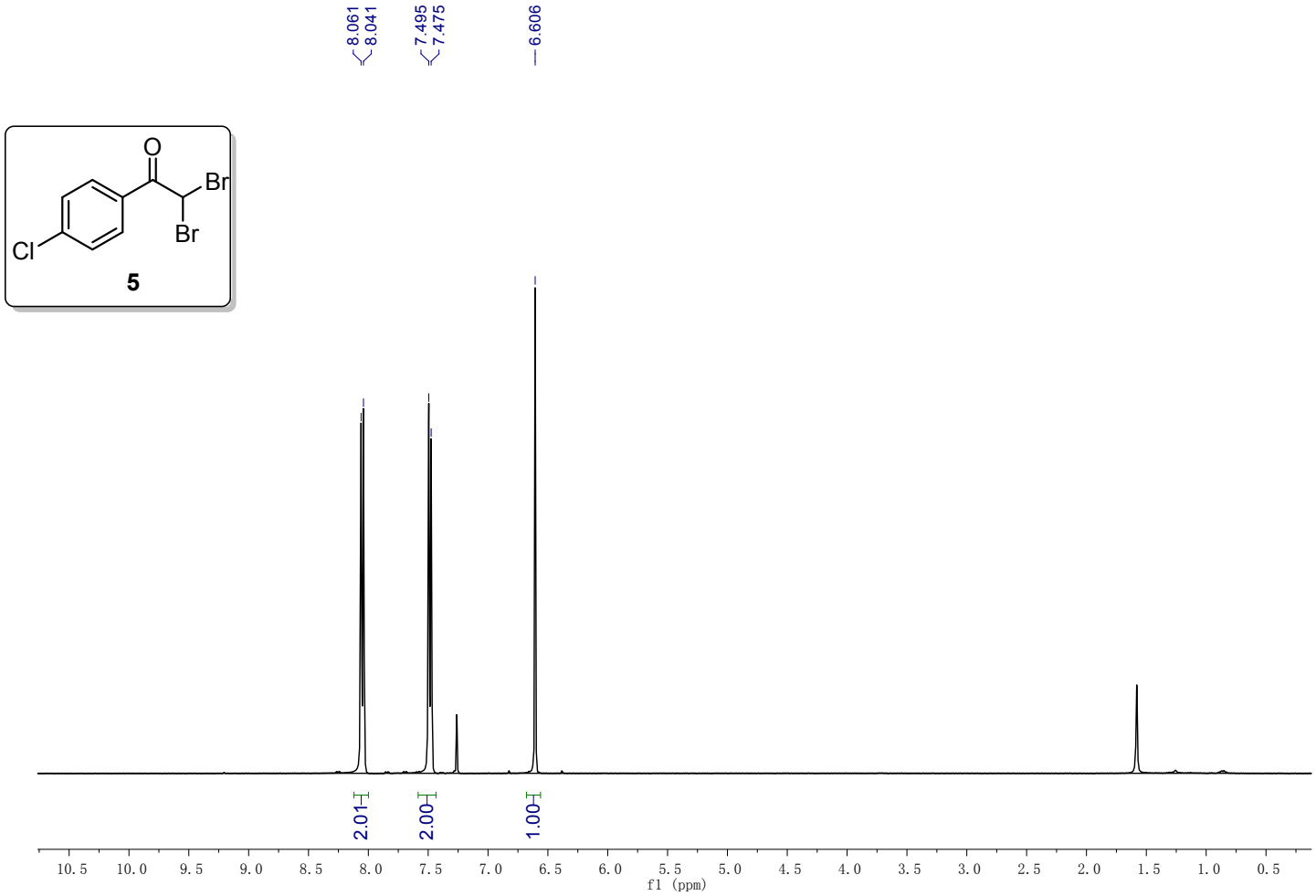
**$^{13}$C NMR of 4**


184.570
167.636
165.072
132.743
132.648
127.124
127.093
116.347
116.127
39.360
O
Br
Br
F
4
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

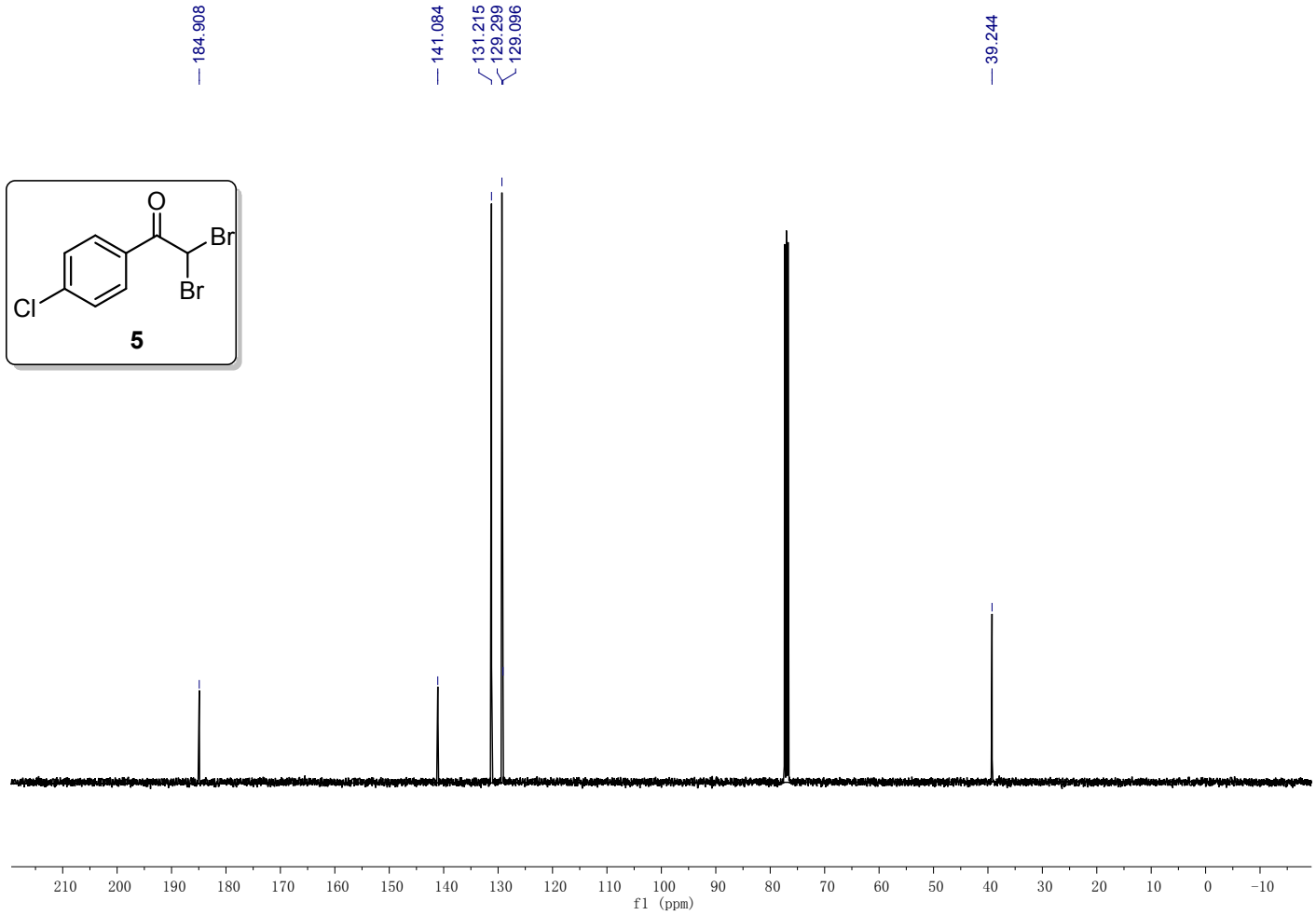
## $^{19}$F NMR of 4


-101.832
-101.841
-101.849
-101.859
-101.869
-101.878
-101.885
-101.897
-101.908
O
Br
Br
F
4
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

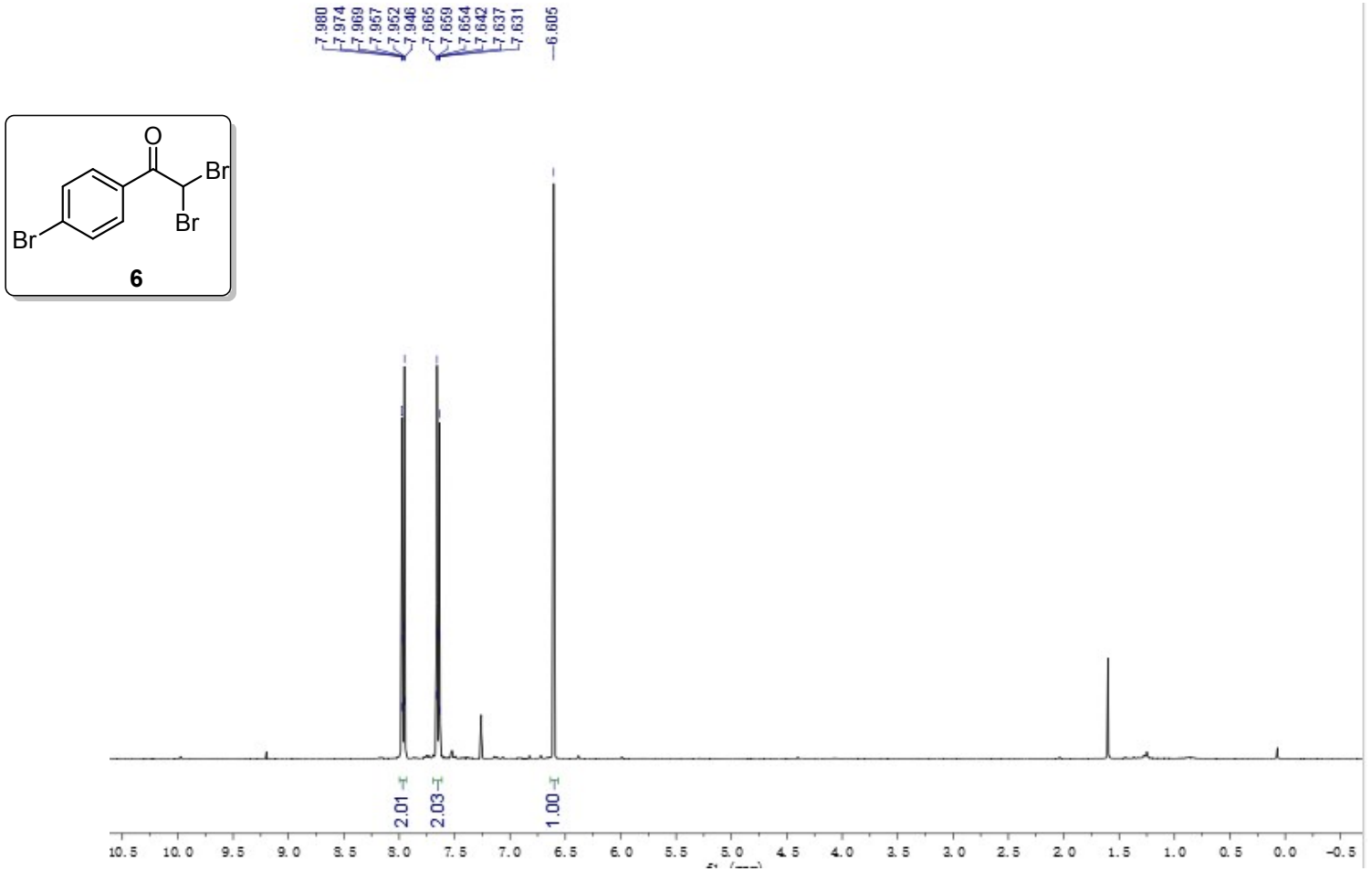
## $^{1}$H NMR of 5


8.061
8.041
7.495
7.475
6.606
O
Br
Br
Cl
5
2.01
2.00
1.00
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
f1 (ppm)

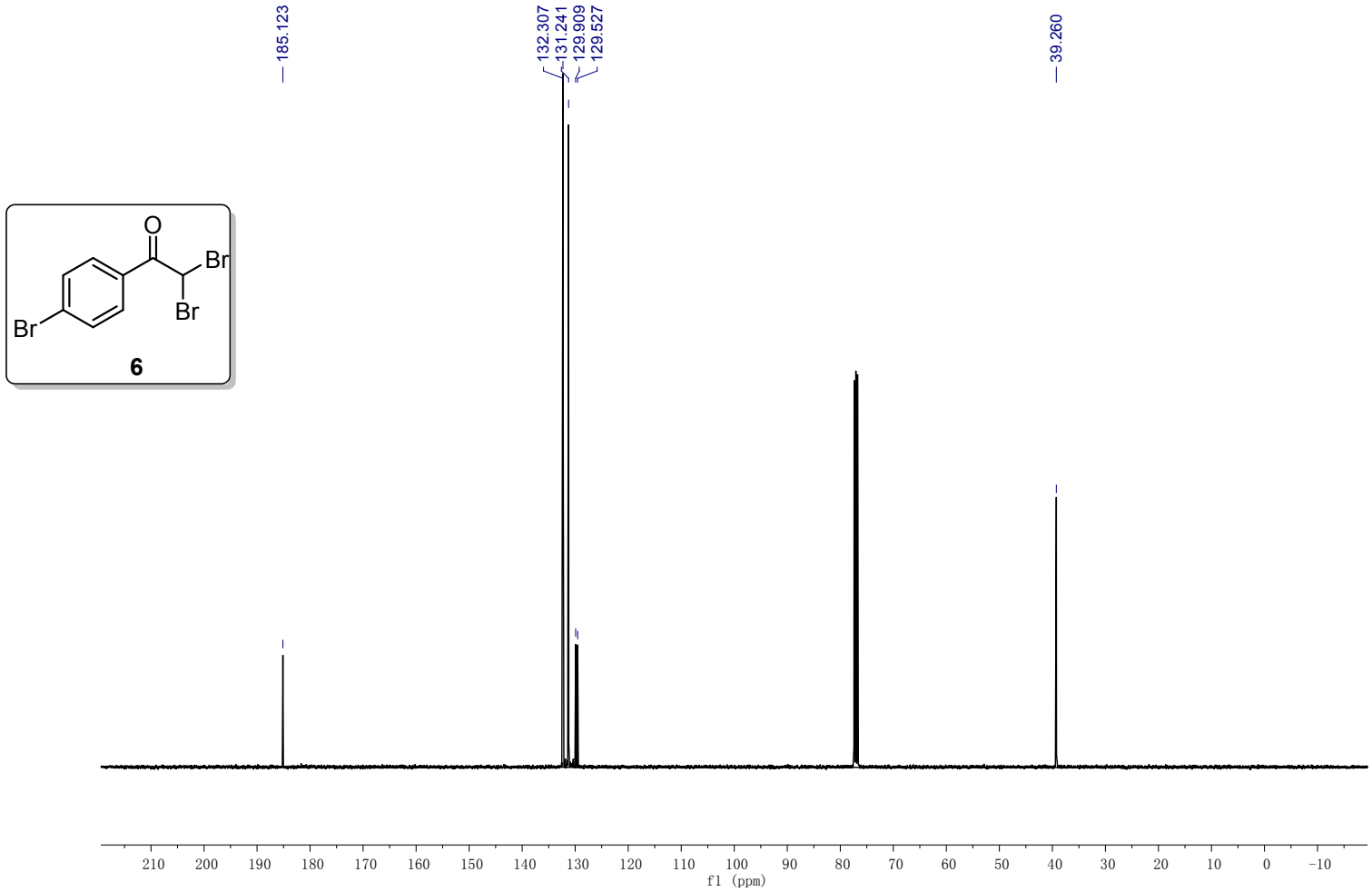
## $^{13}$C NMR of 5


184.908
141.084
131.215
129.299
129.096
39.244
O
Br
Br
Cl
5
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)

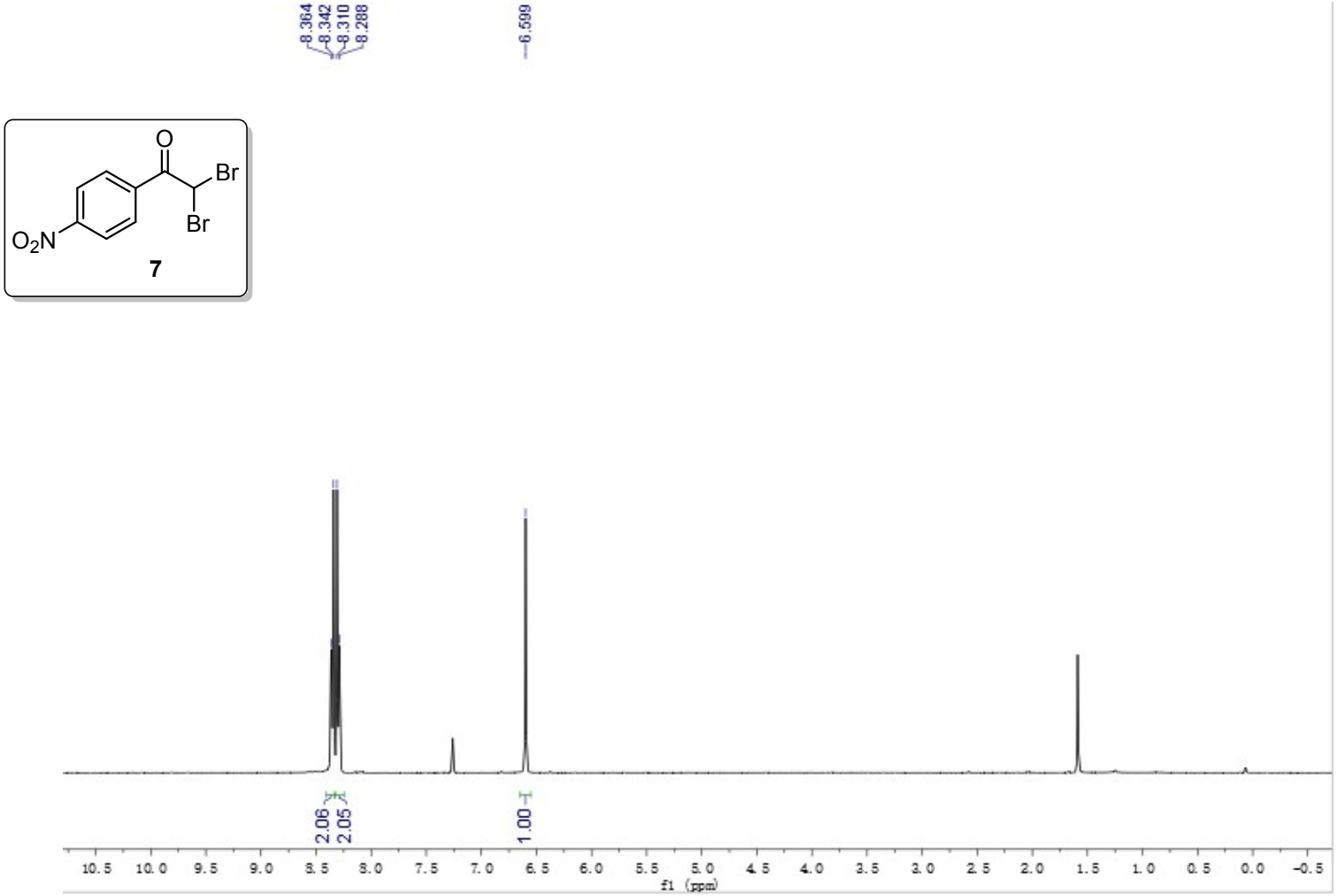
**$^{1}$H NMR of 6**


7.980
7.974
7.969
7.957
7.952
7.946
7.665
7.659
7.654
7.642
7.637
7.631
6.605
O
Br
Br
Br
6
2.01
2.03
1.00
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

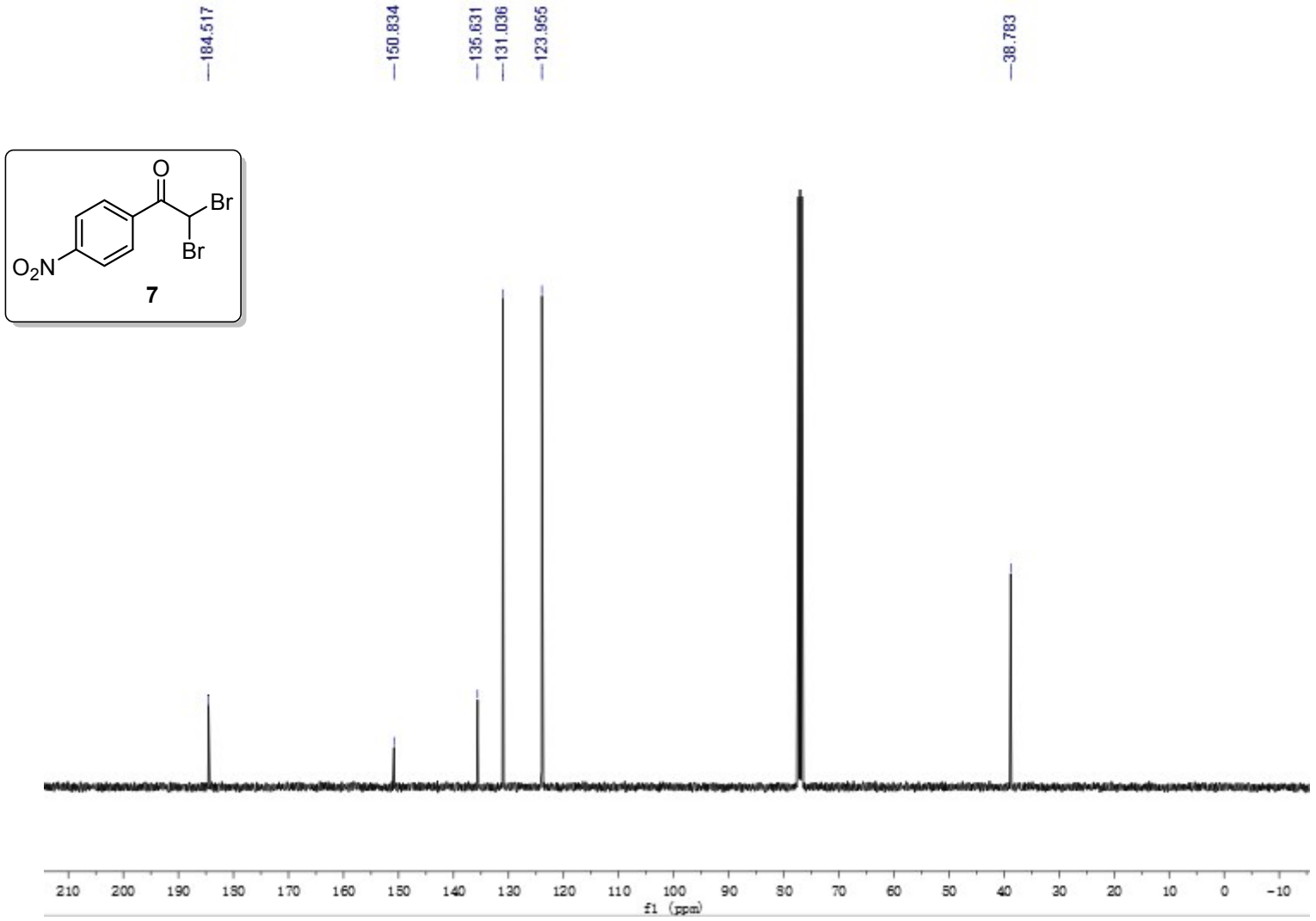
## $^{13}$C NMR of 6


185.123
132.307
131.241
129.909
129.527
39.260
O
Br
Br
Br
6
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)

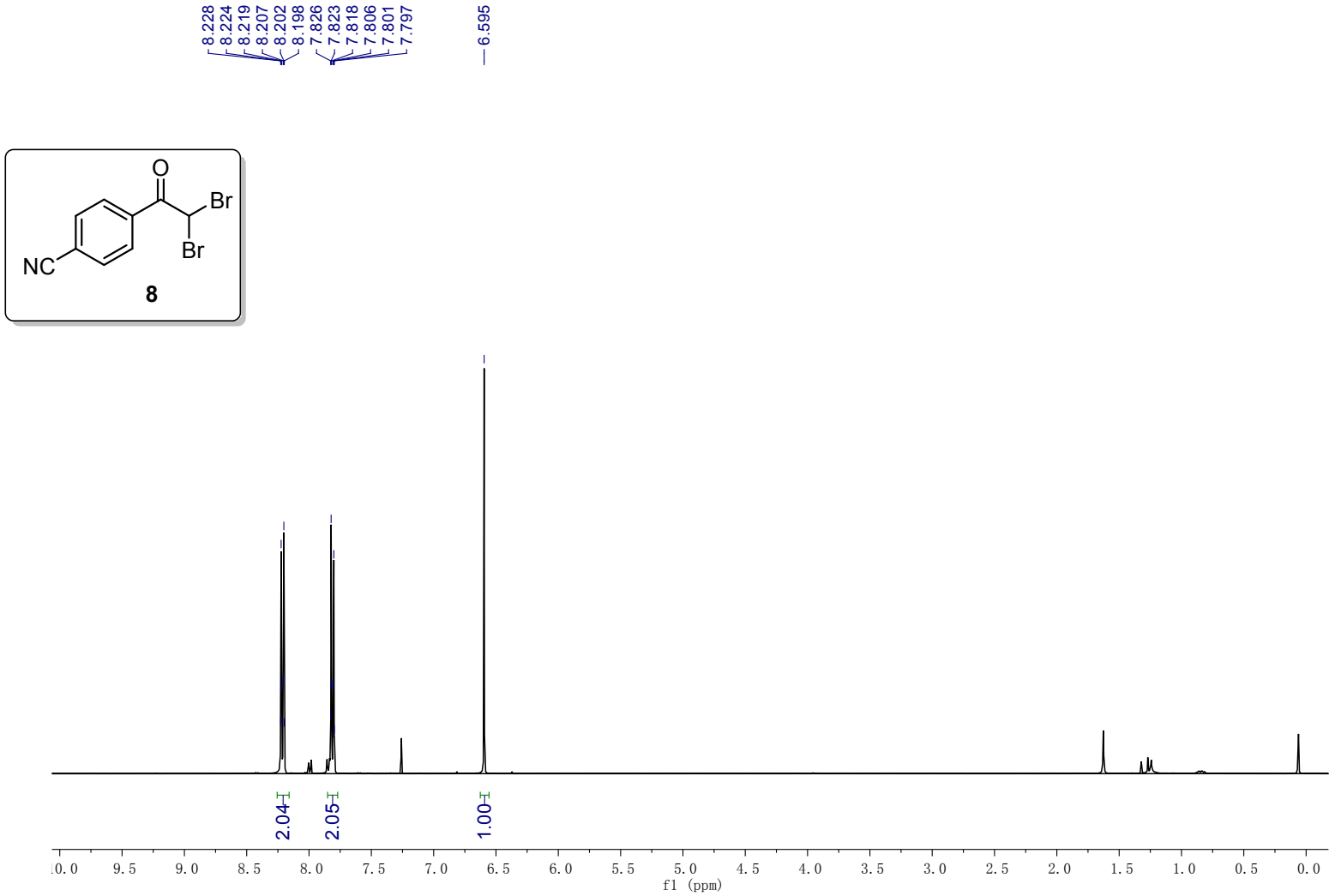
**$^1$H NMR of 7**


8.364
8.342
8.310
8.288
6.599
O
Br
Br
$O_2N$
7
2.06
2.05
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

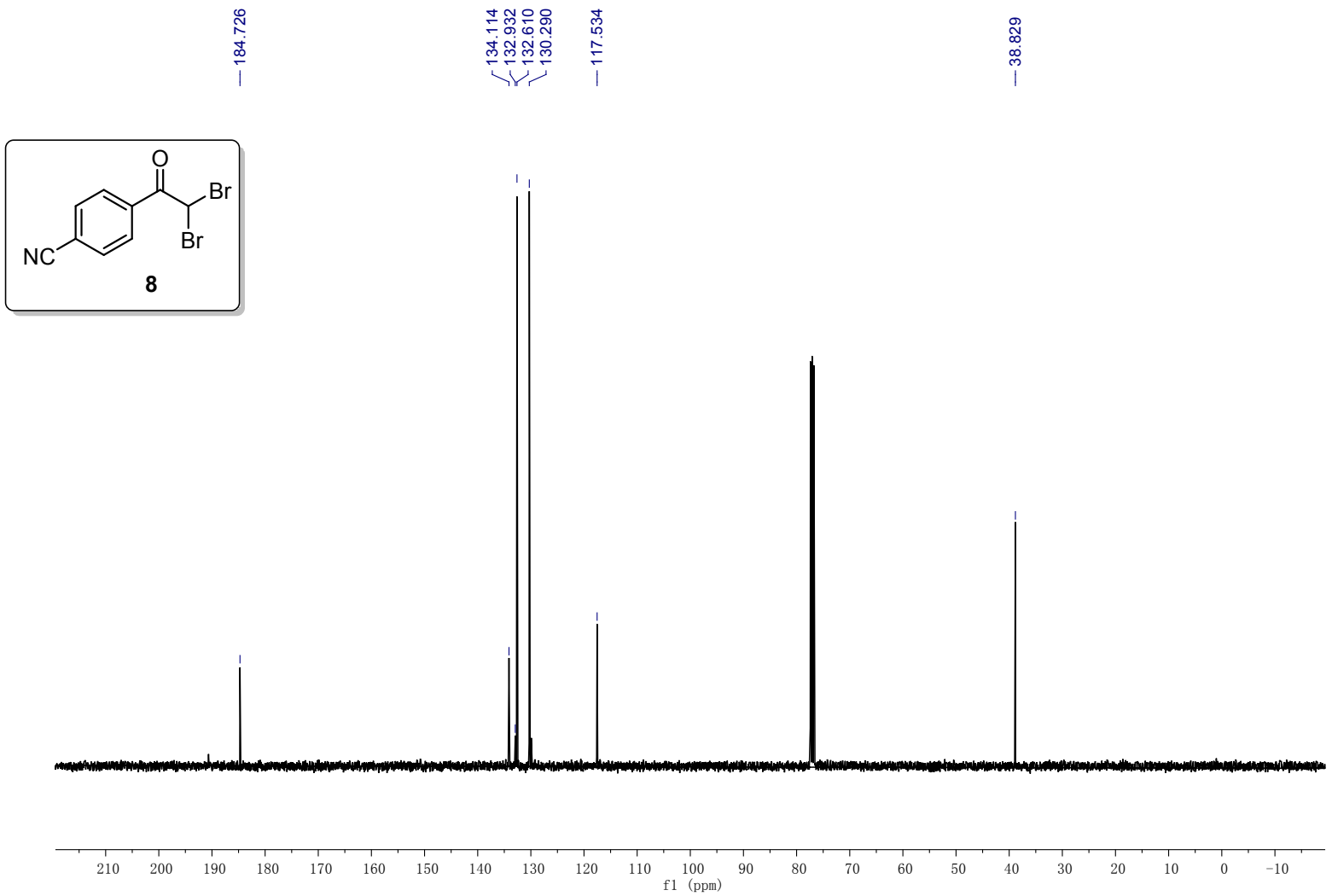
**$^{13}$C NMR of 7**


184.517
150.834
135.631
131.036
123.955
38.783
O
Br
Br
$O_2N$
7
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)

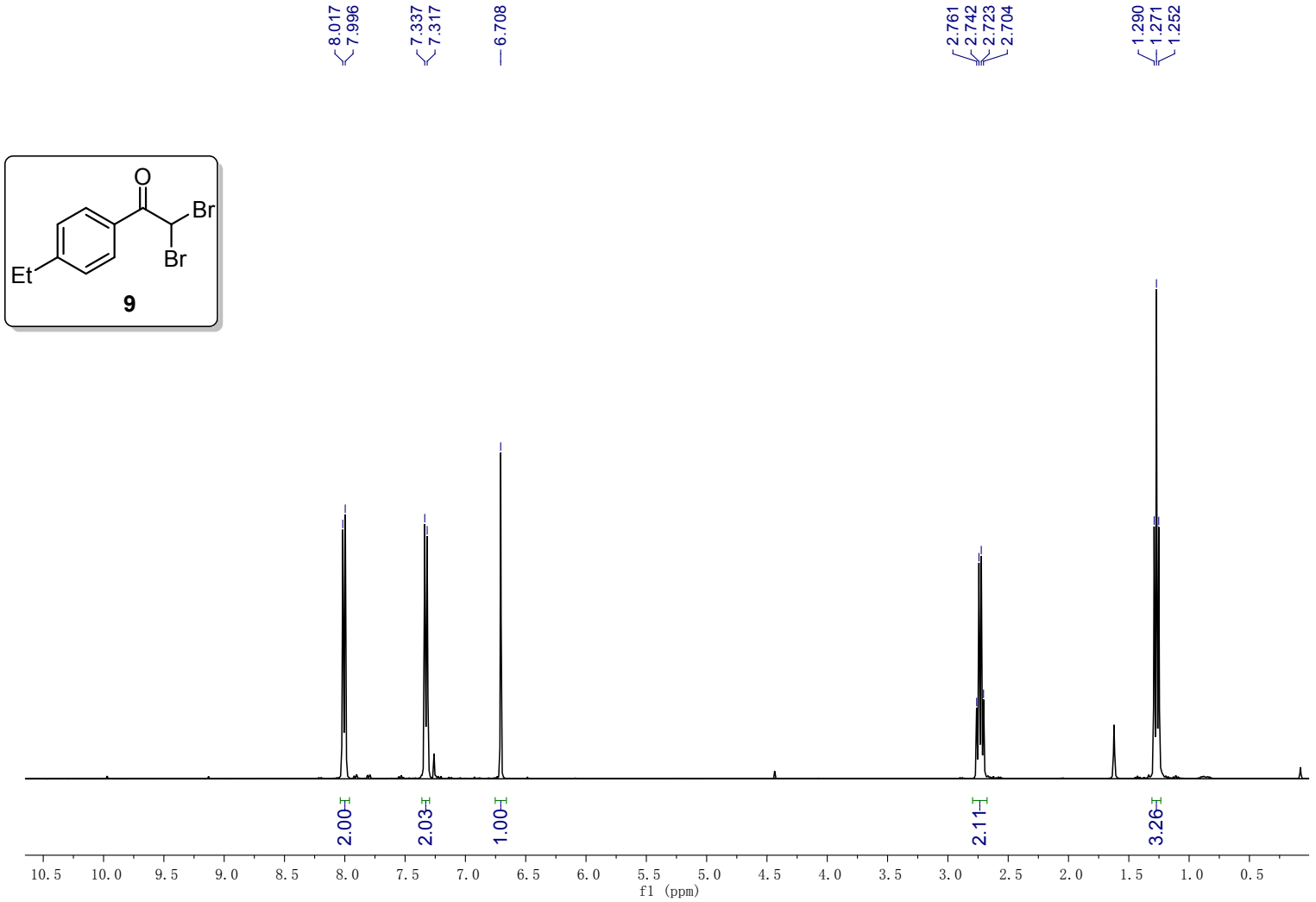
## $^1$H NMR of 8


8.228
8.224
8.219
8.207
8.202
8.198
7.826
7.823
7.818
7.806
7.801
7.797
6.595
O
Br
Br
NC
8
2.04
2.05
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

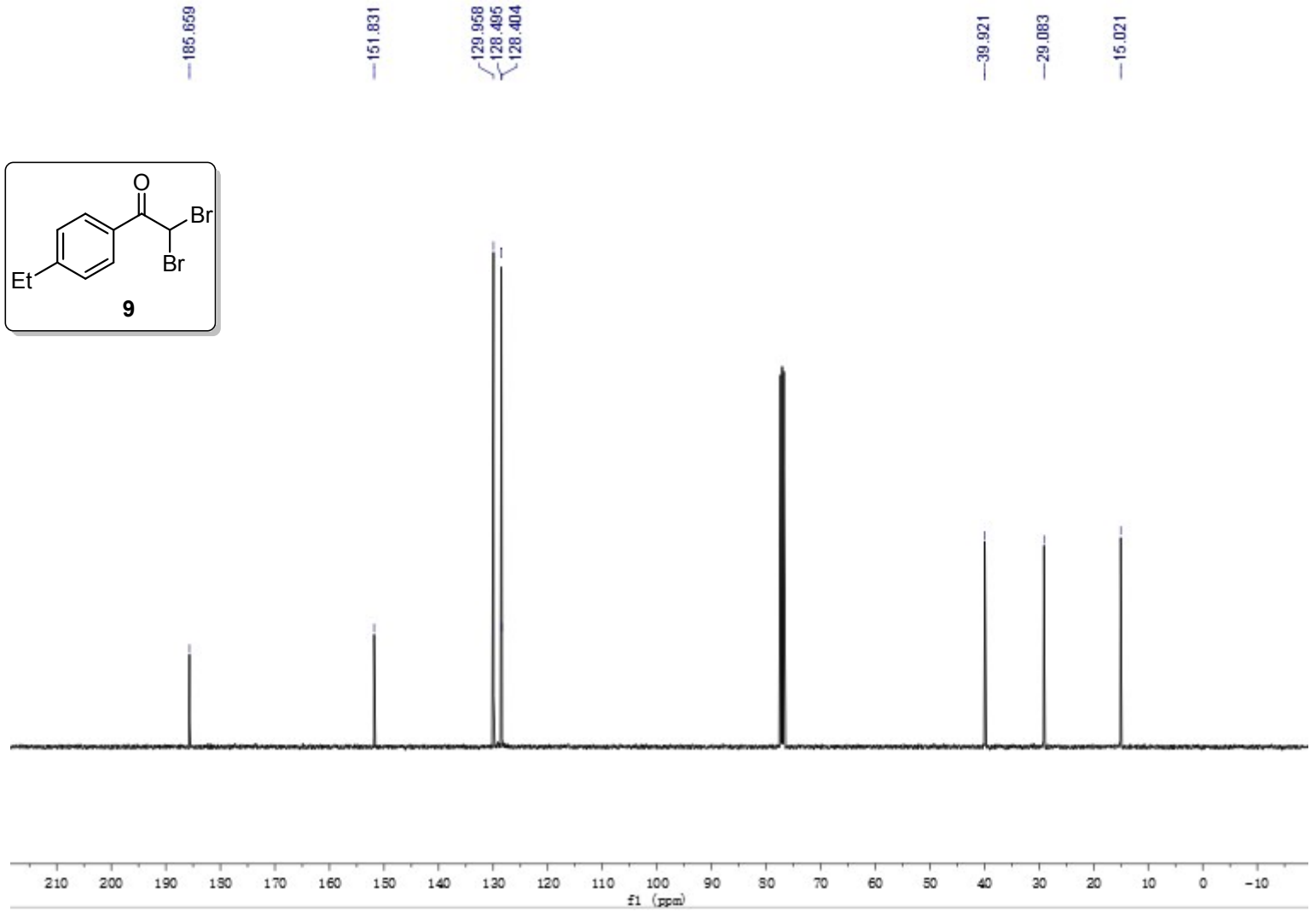
## $^{13}$C NMR of 8


184.726
134.114
132.932
132.610
130.290
117.534
38.829
O
Br
Br
NC
8
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)

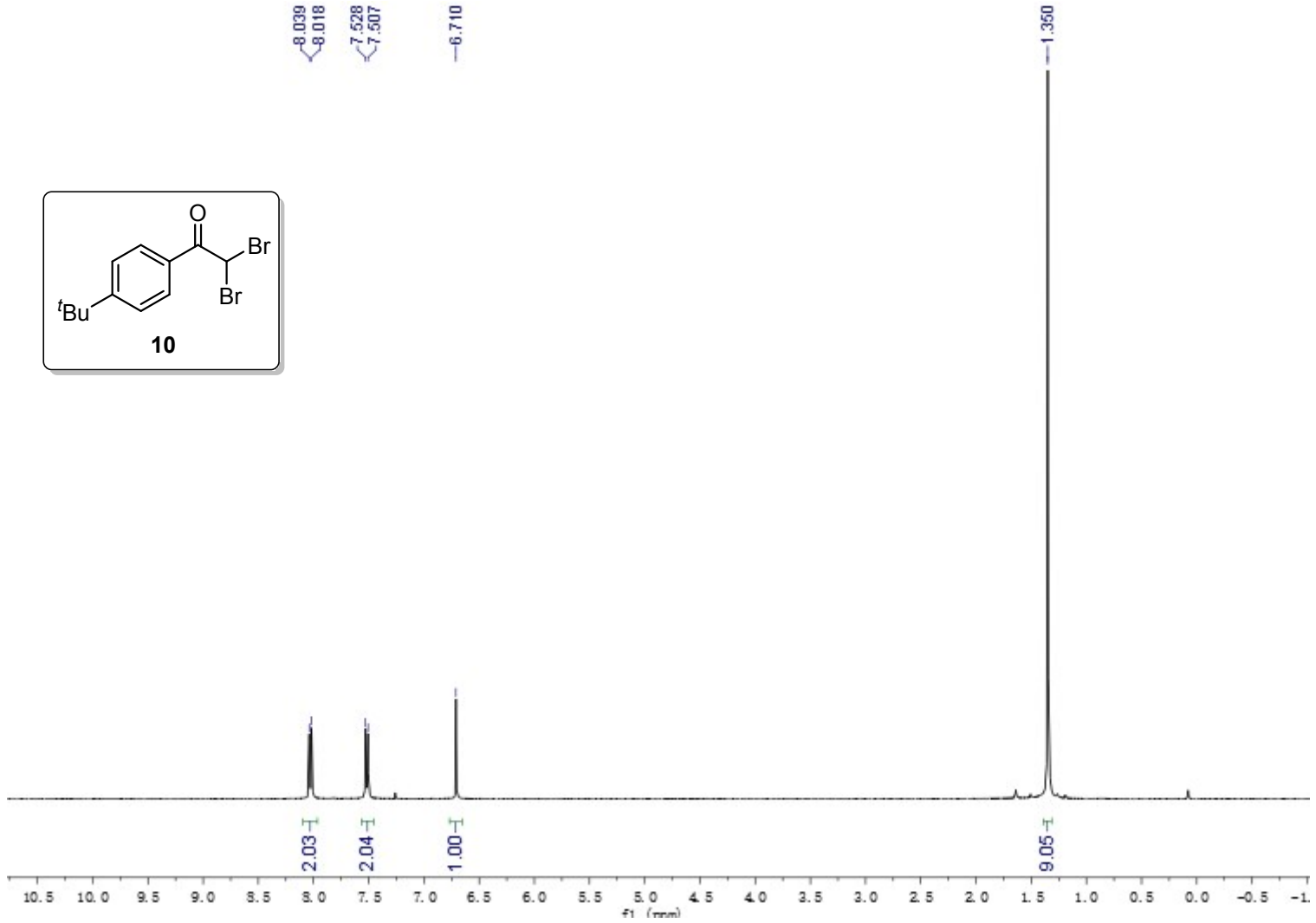
## $^1$H NMR of 9


8.017
7.996
7.337
7.317
6.708
2.761
2.742
2.723
2.704
1.290
1.271
1.252
O
Br
Br
Et
9
2.00
2.03
1.00
2.11
3.26
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
f1 (ppm)

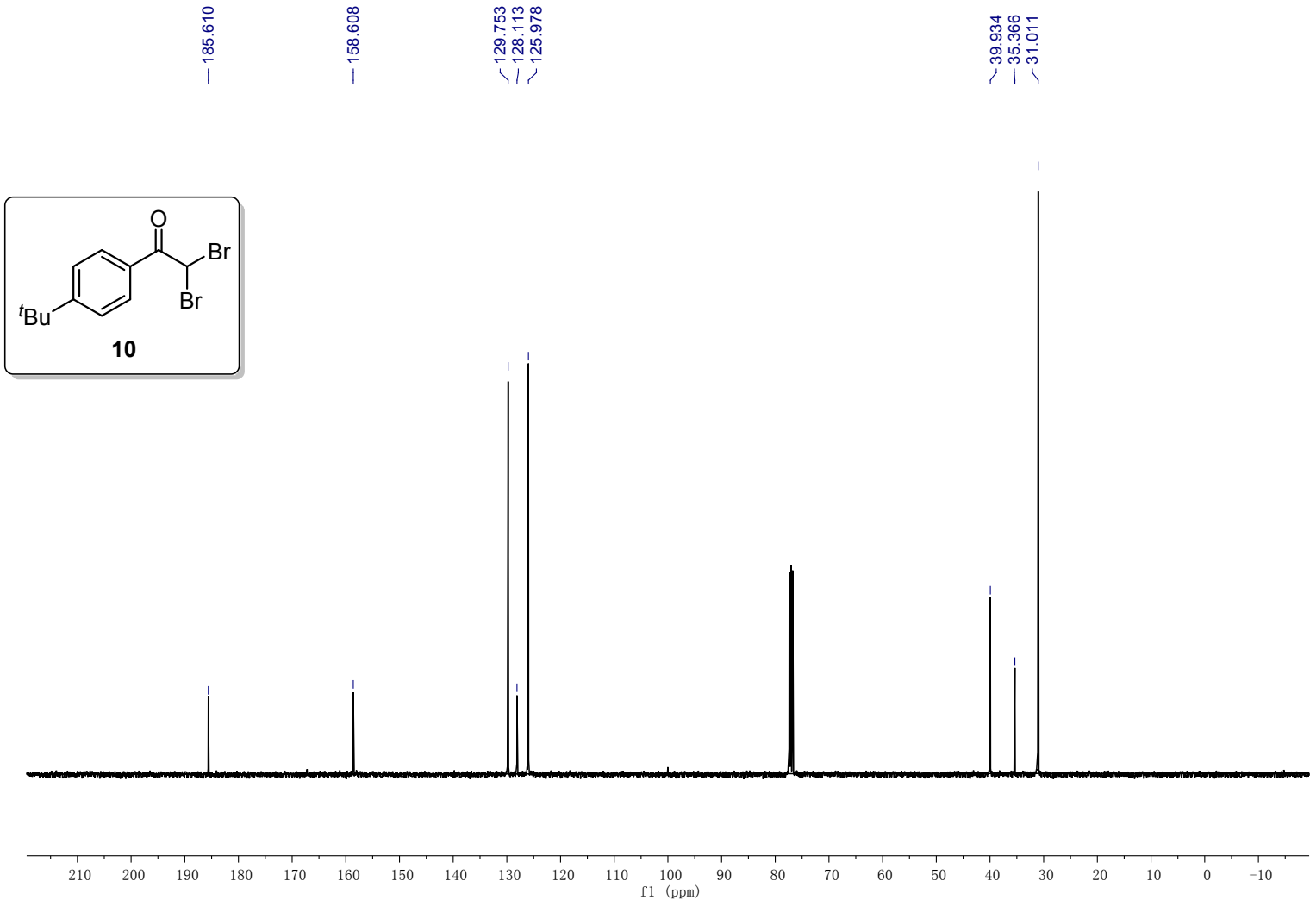
**$^{13}$C NMR of 9**


185.659
151.831
129.958
128.495
128.404
39.921
29.083
15.021
O
Br
Br
Et
9
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)

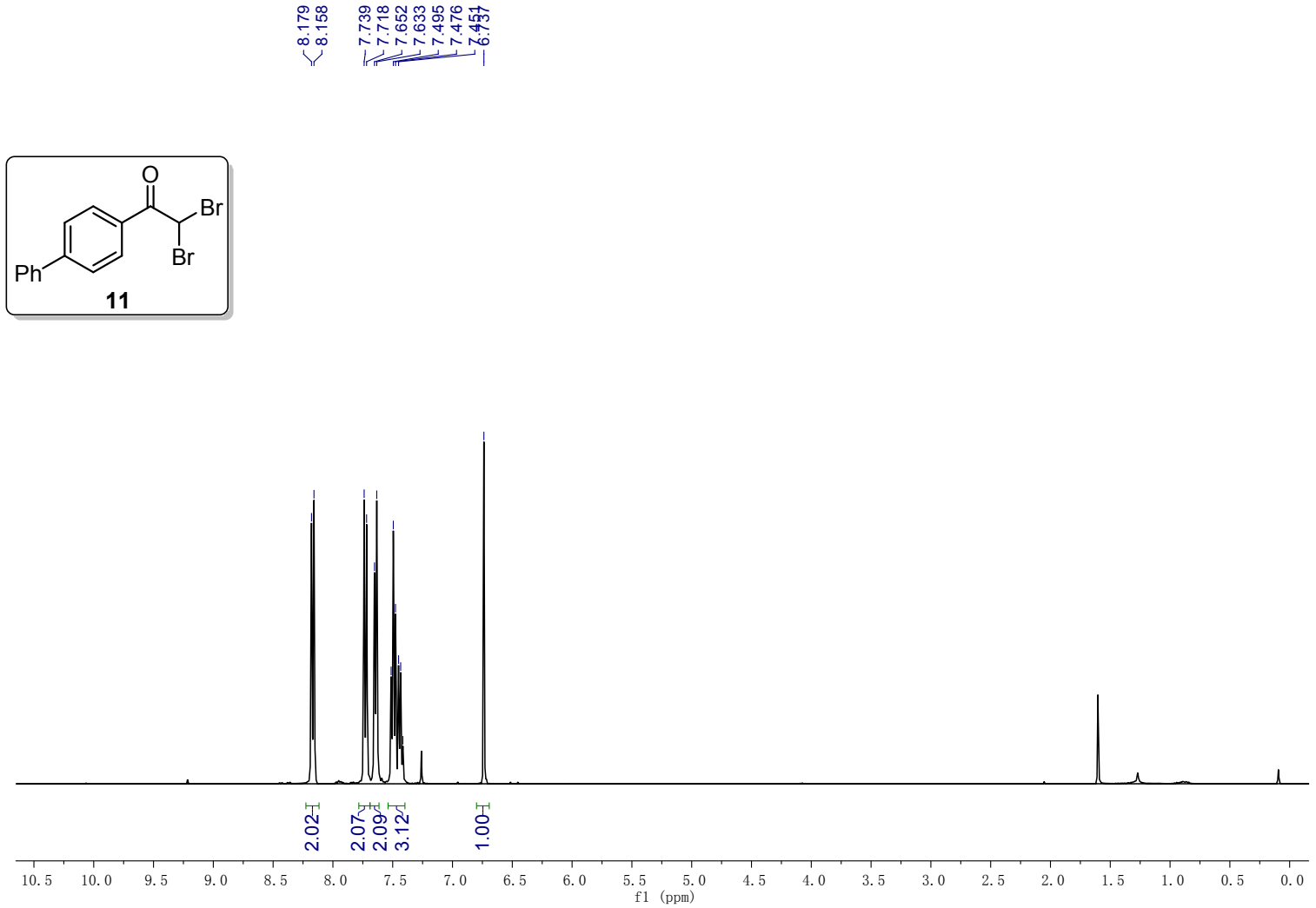
**$^1$H NMR of 10**


8.039
8.018
7.528
7.507
6.710
1.350
O
Br
Br
tBu
10
2.03
2.04
1.00
9.05
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)

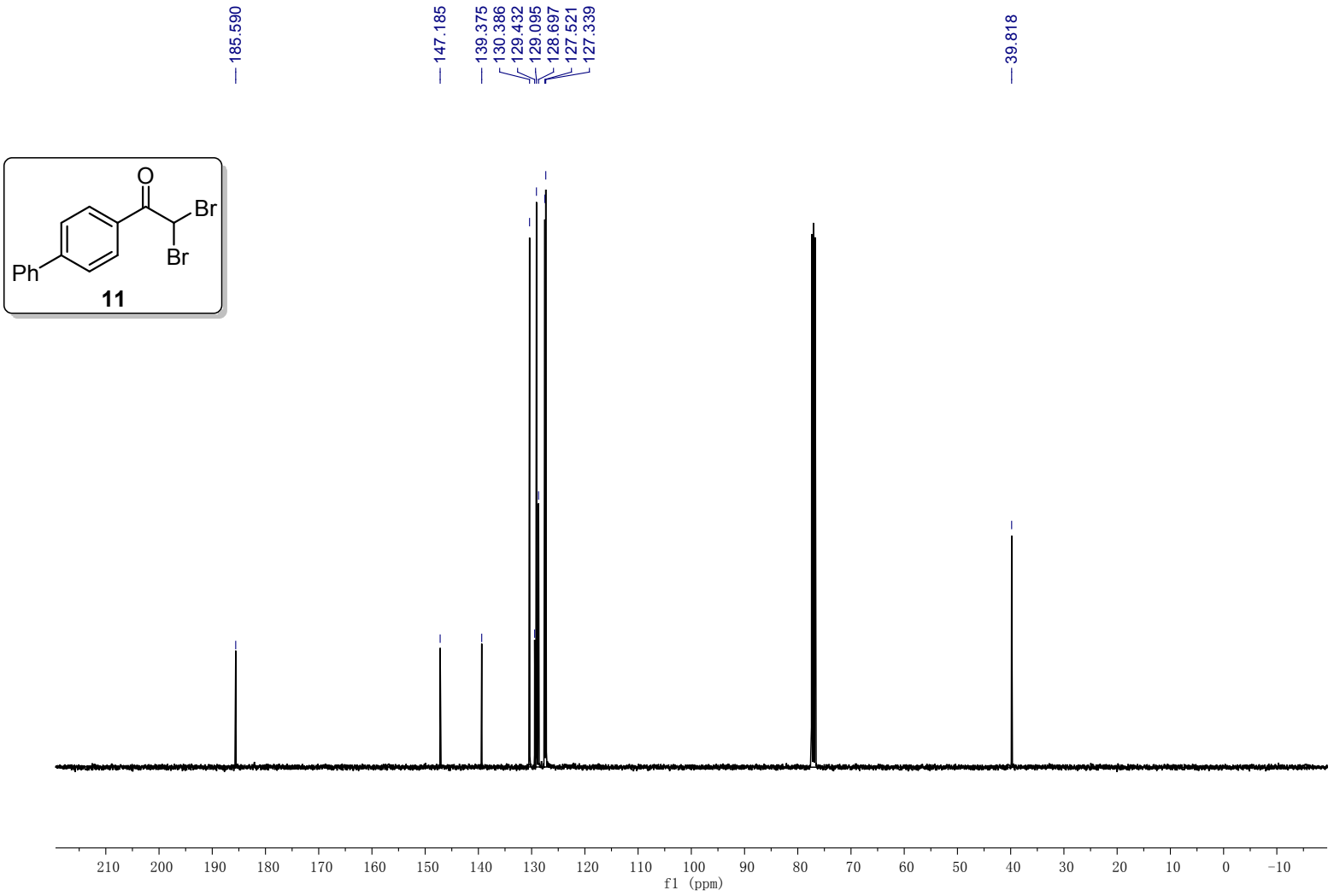
## $^{13}$C NMR of 10


185.610
158.608
129.753
128.113
125.978
39.934
35.366
31.011
O
Br
Br
tBu
10
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)

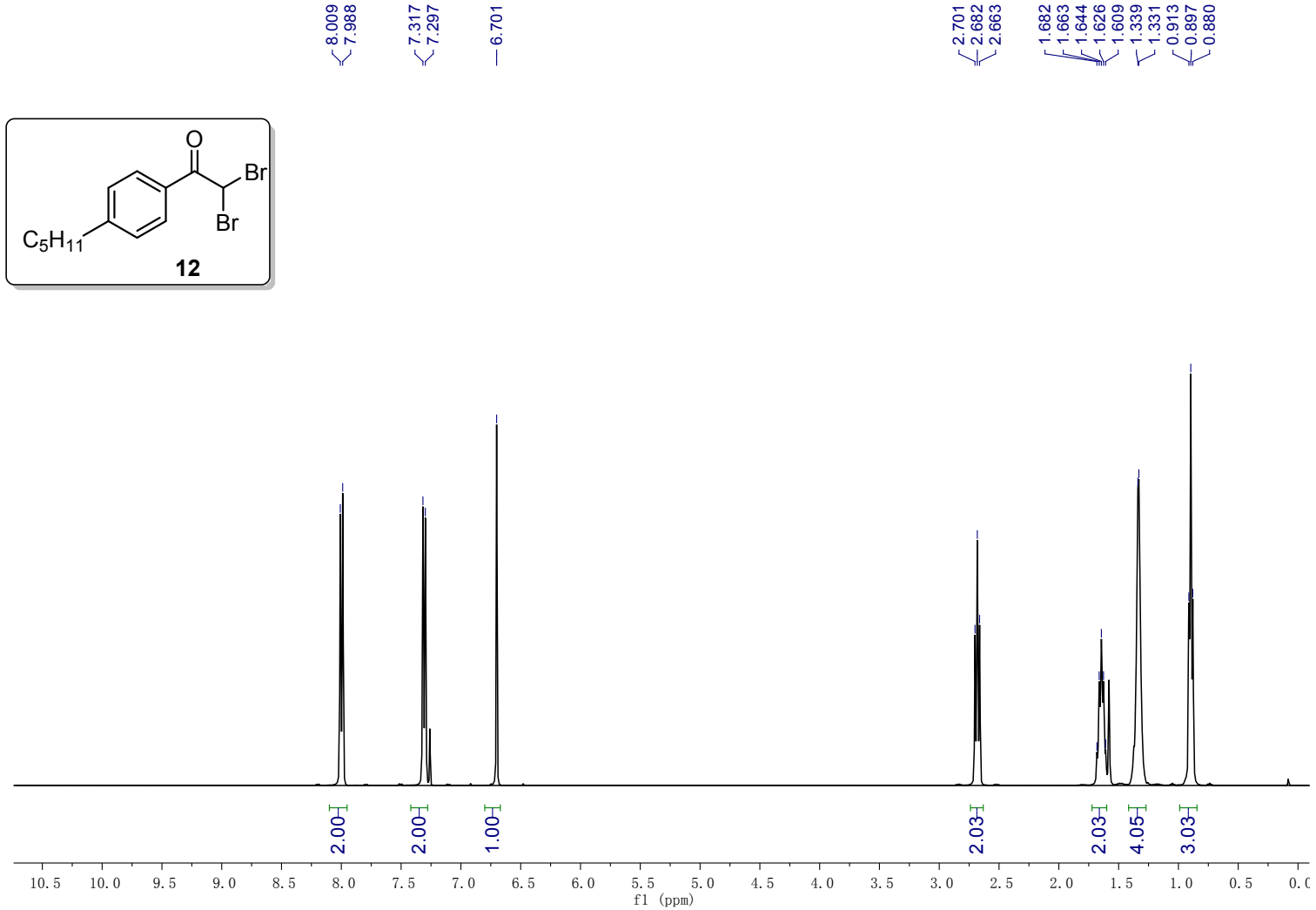
## $^{1}$H NMR of 11


8.179
8.158
7.739
7.718
7.652
7.633
7.495
7.476
7.451
7.437
O
Br
Br
Ph
11
2.02
2.07
2.09
3.12
1.00
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
f1 (ppm)

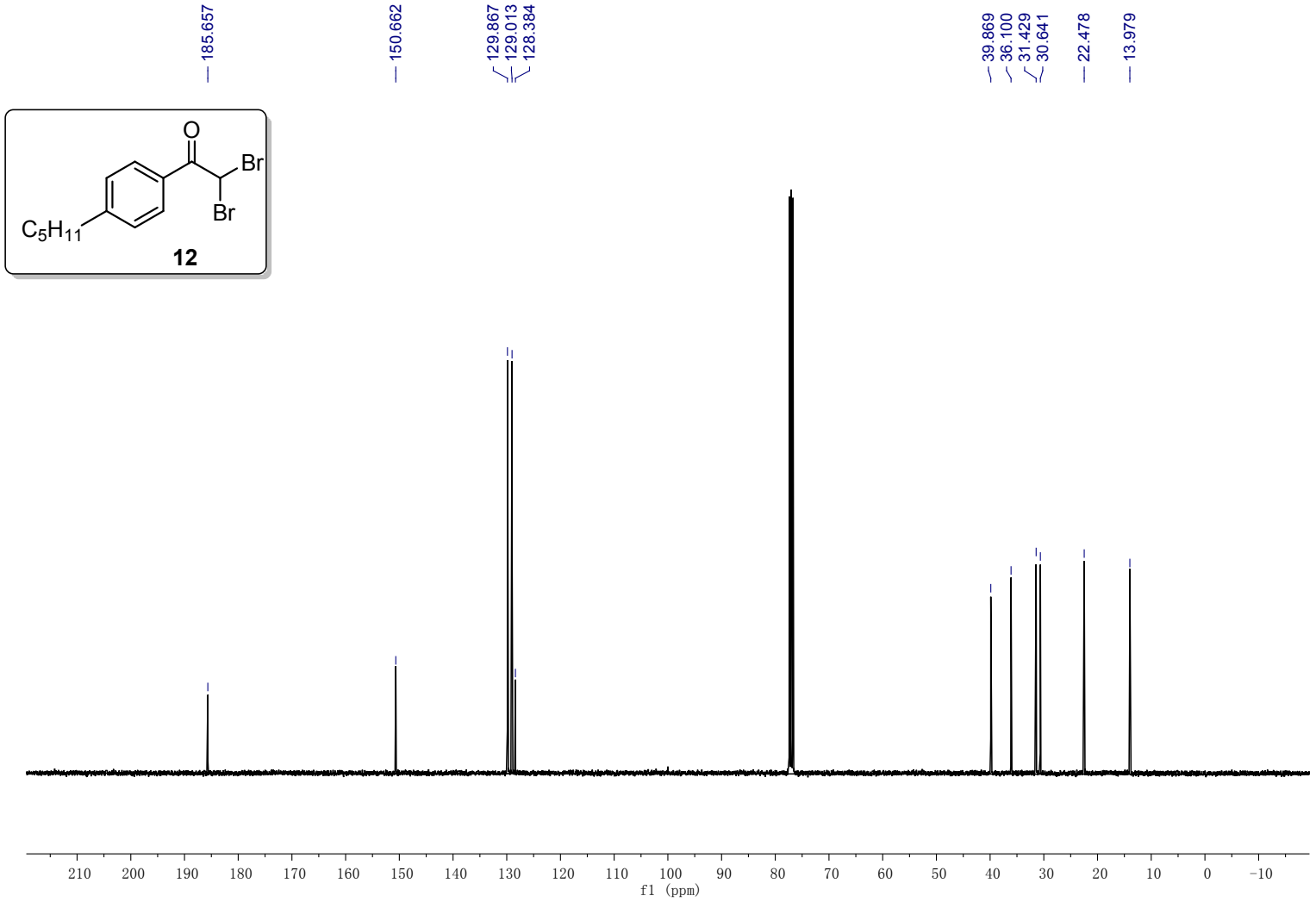
## $^{13}$C NMR of 11


185.590
147.185
139.375
130.386
129.432
129.095
128.697
127.521
127.339
39.818
O
Br
Br
Ph
11
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)

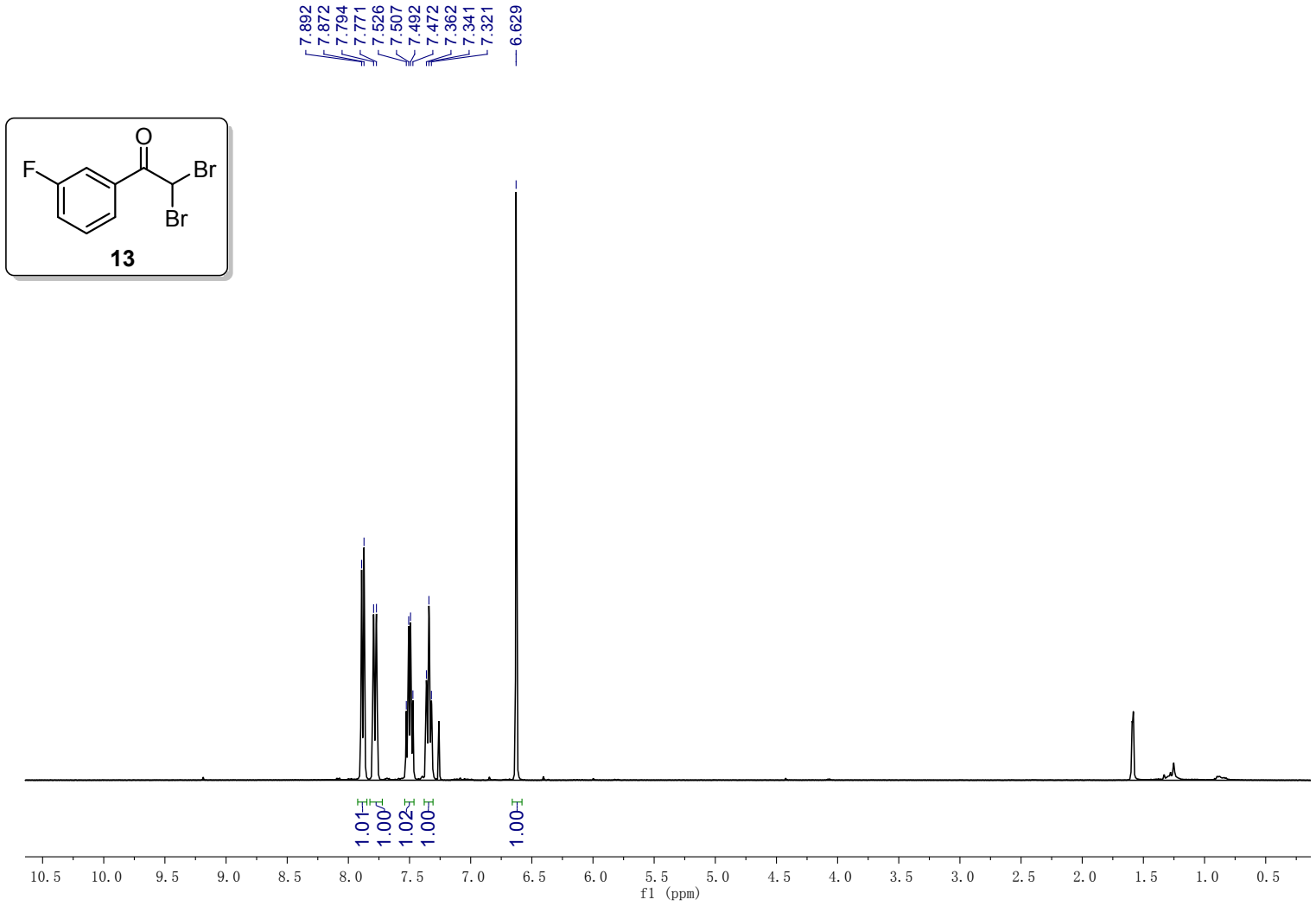
## $^1$H NMR of 12


8.009
7.988
7.317
7.297
6.701
2.701
2.682
2.663
1.682
1.663
1.644
1.626
1.609
1.339
1.331
0.913
0.897
0.880
O
Br
Br
C5H11
12
2.00
2.00
1.00
2.03
2.03
4.05
3.03
f1 (ppm)

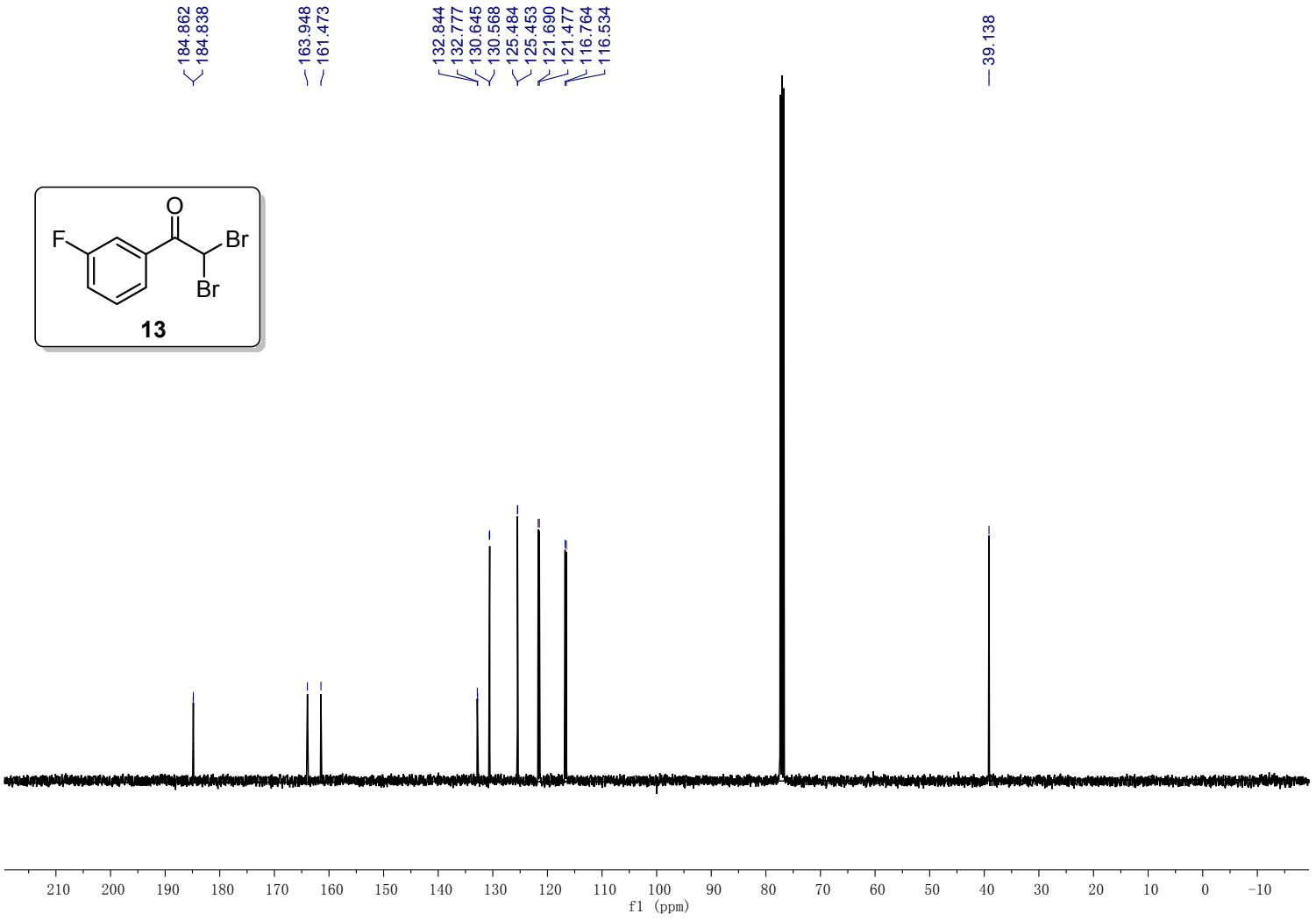
## $^{13}$C NMR of 12


185.657
150.662
129.867
129.013
128.384
39.869
36.100
31.429
30.641
22.478
13.979
O
Br
Br
C5H11
12
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)

## $^1$H NMR of 13


7.892
7.872
7.794
7.771
7.526
7.507
7.492
7.472
7.362
7.341
7.321
6.629
O
F
Br
Br
13
1.01
1.00
1.02
1.00
1.00
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
f1 (ppm)

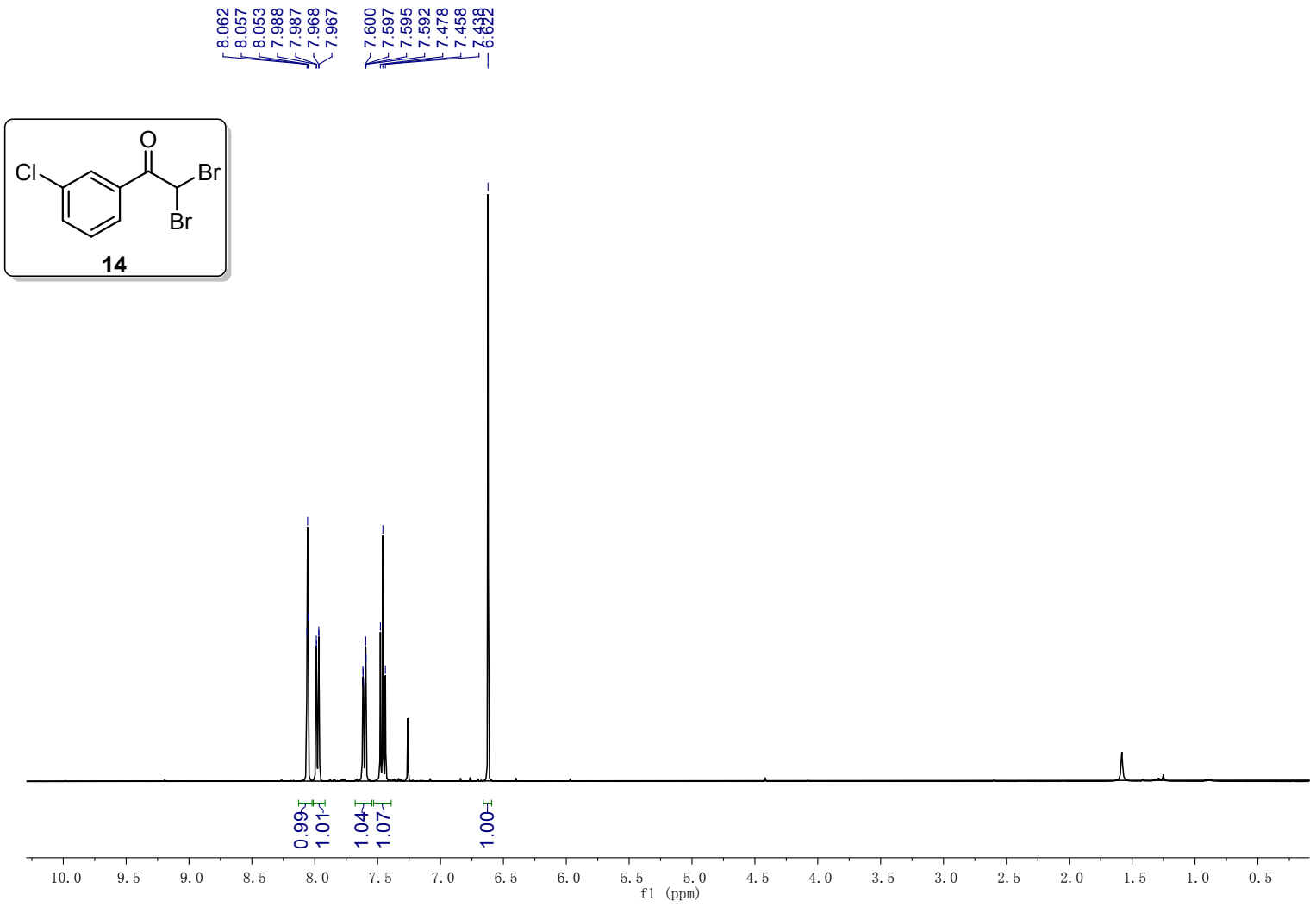
## $^{13}$C NMR of 13


184.862
184.838
163.948
161.473
132.844
132.777
130.645
130.568
125.484
125.453
121.690
121.477
116.764
116.534
39.138
O
F
Br
Br
13
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)

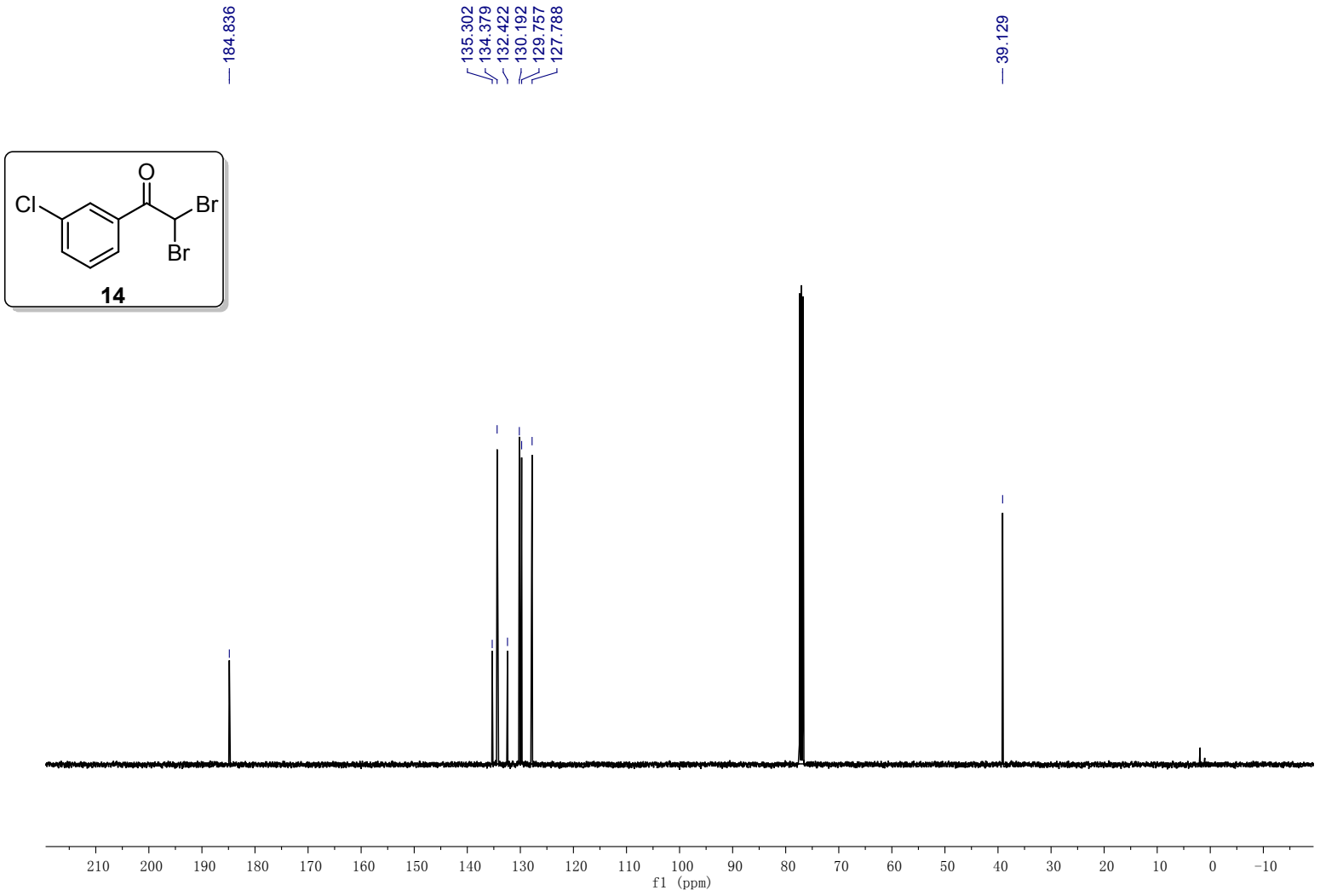
## $^{19}$F NMR of 13


-101.832
-101.841
-101.849
-101.859
-101.869
-101.878
-101.885
-101.897
-101.908
F
O
Br
Br
13
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

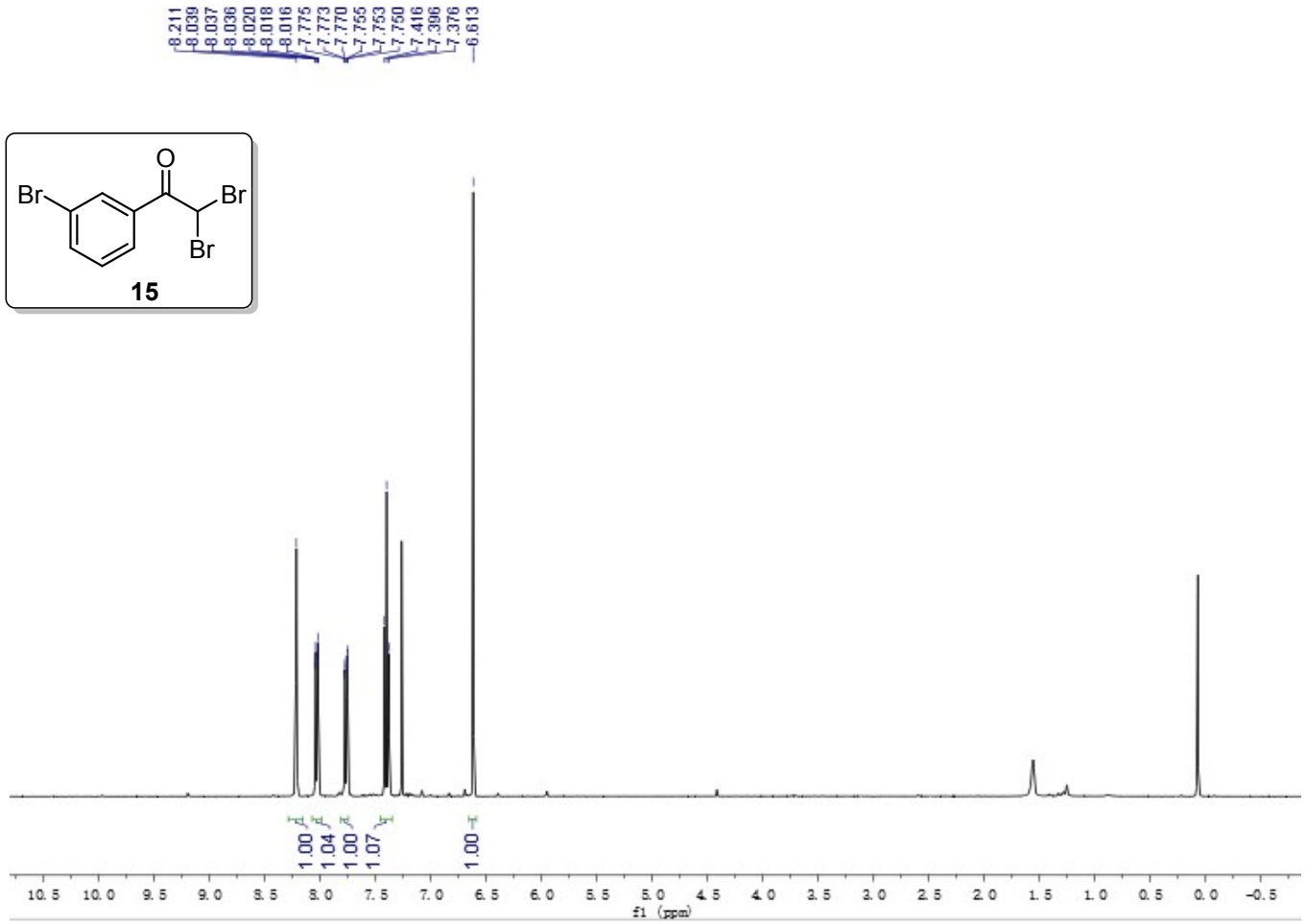
## $^{1}$H NMR of 14


8.062
8.057
8.053
7.988
7.987
7.968
7.967
7.600
7.597
7.595
7.592
7.478
7.458
7.438
7.422
6.622
O
Cl
Br
Br
14
0.99
1.01
1.04
1.07
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

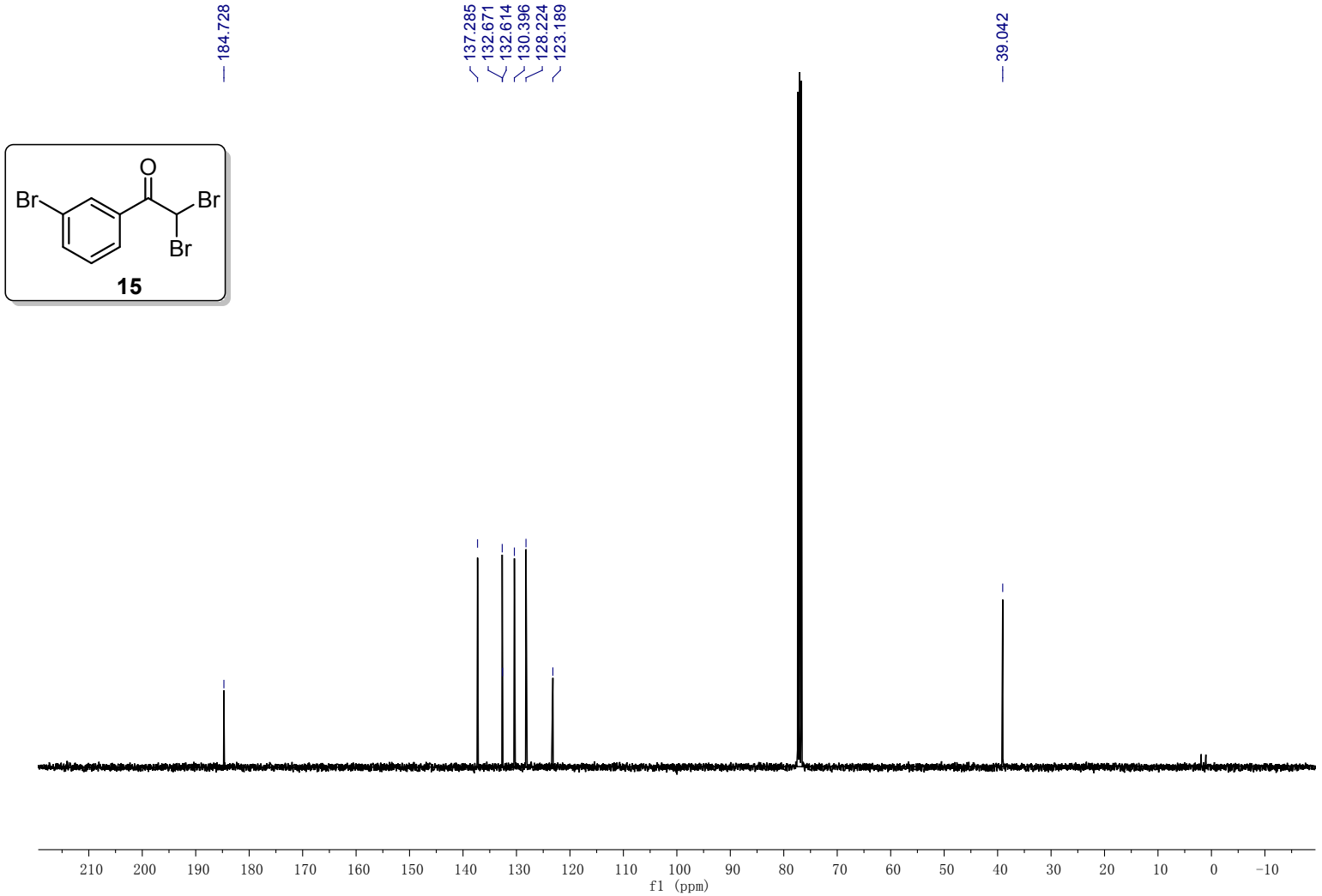
## $^{13}$C NMR of 14


184.836
135.302
134.379
132.422
130.192
129.757
127.788
39.129
O
Cl
Br
Br
14
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)

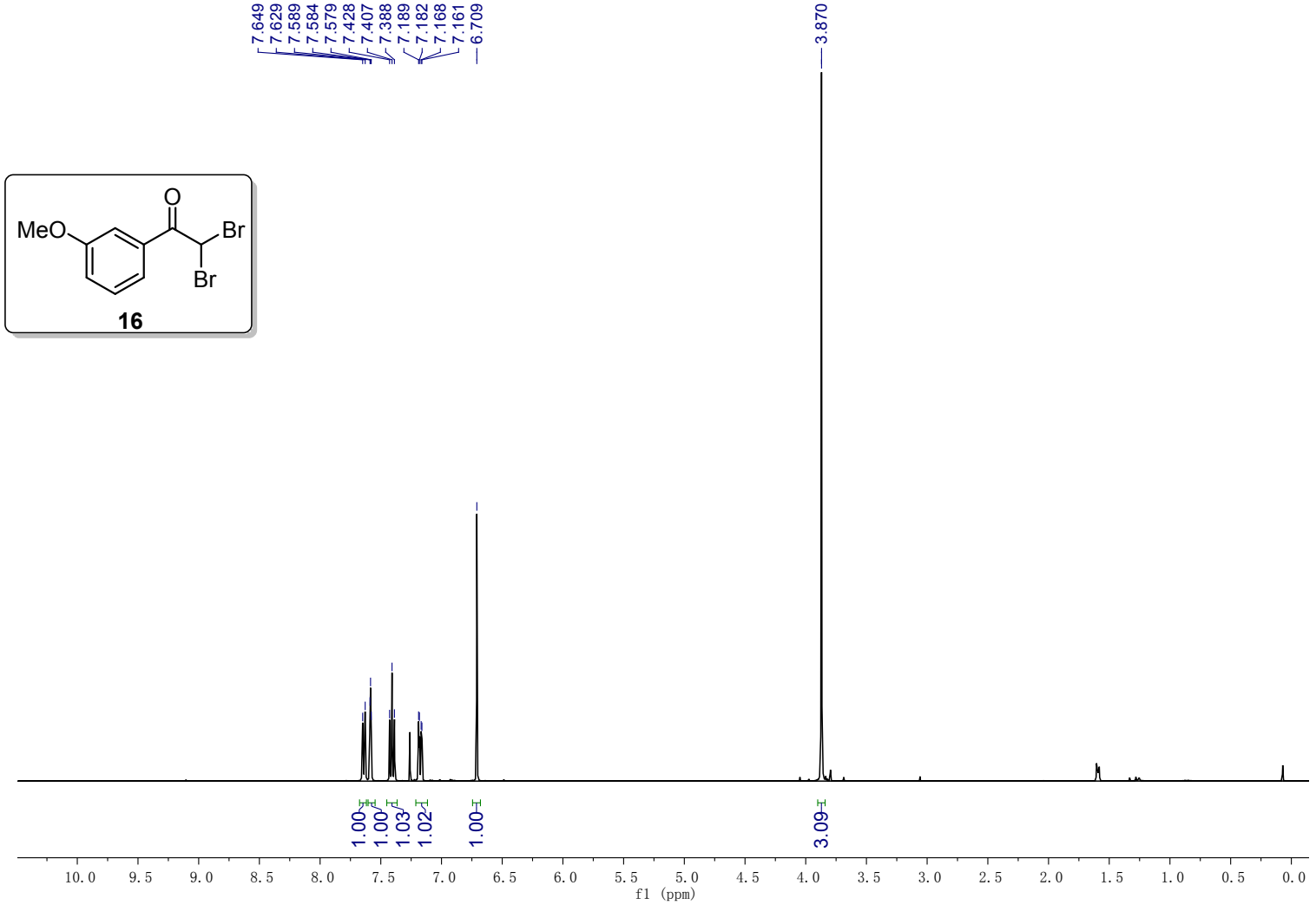
## $^{1}$H NMR of 15


8.211
8.039
8.037
8.036
8.020
8.018
8.016
7.775
7.773
7.770
7.755
7.753
7.750
7.416
7.396
7.376
6.613
O
Br
Br
Br
15
1.00
1.04
1.00
1.07
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

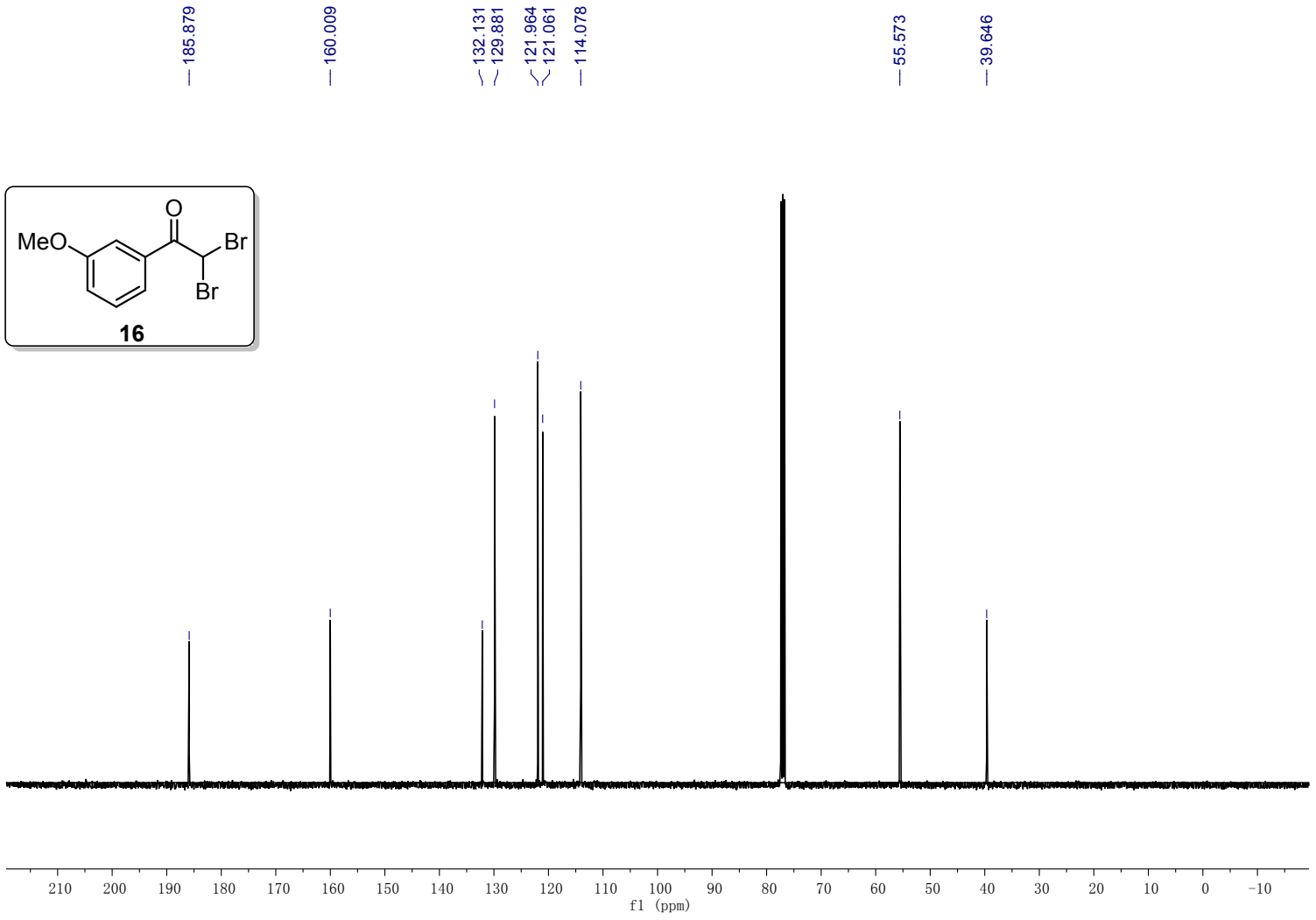
## $^{13}$C NMR of 15


184.728
137.285
132.671
132.614
130.396
128.224
123.189
39.042
O
Br
Br
Br
15
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)

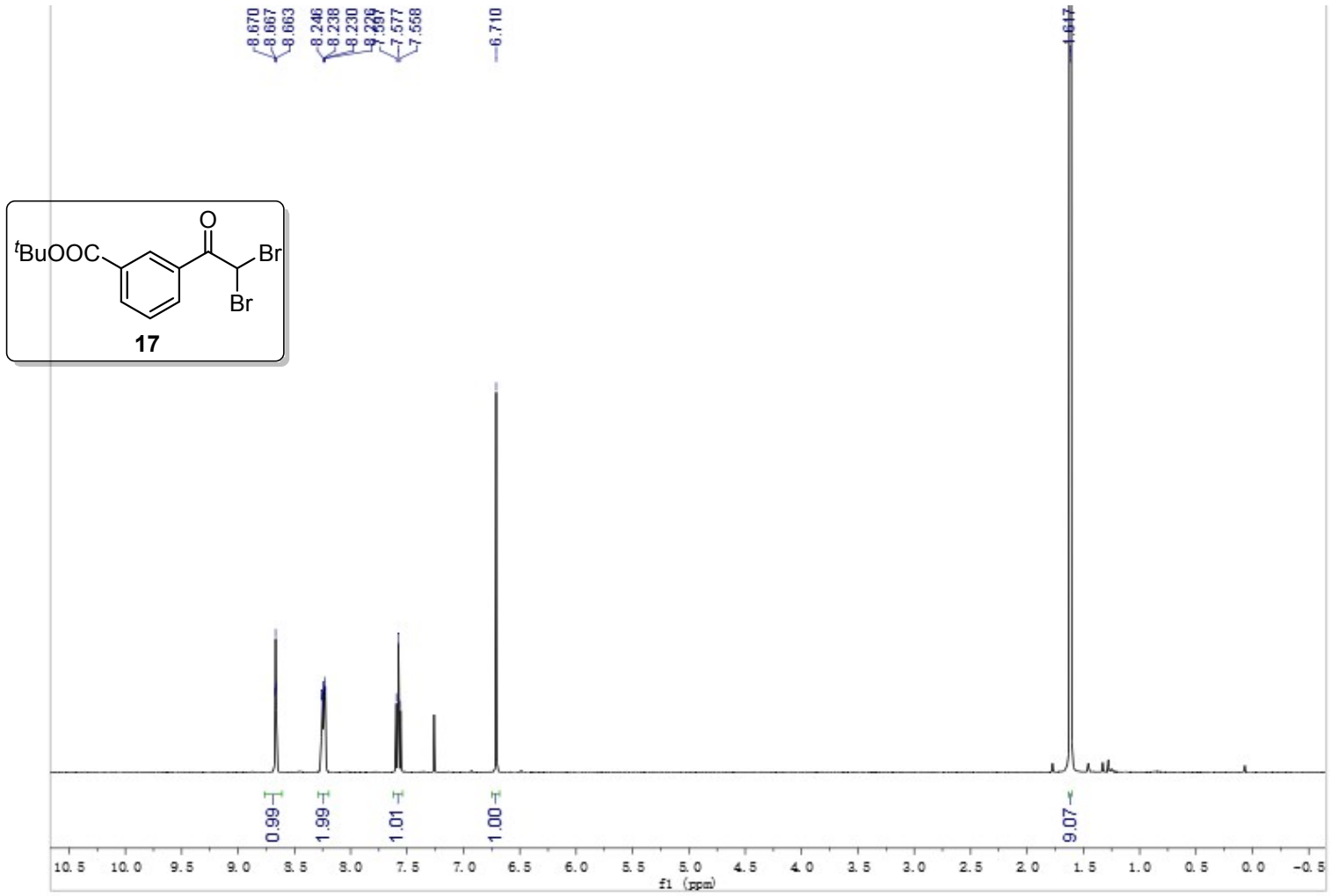
## $^{1}$H NMR of 16


7.649
7.629
7.589
7.584
7.579
7.428
7.407
7.388
7.189
7.182
7.168
7.161
6.709
3.870
MeO
O
Br
Br
16
1.00
1.00
1.03
1.02
1.00
3.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

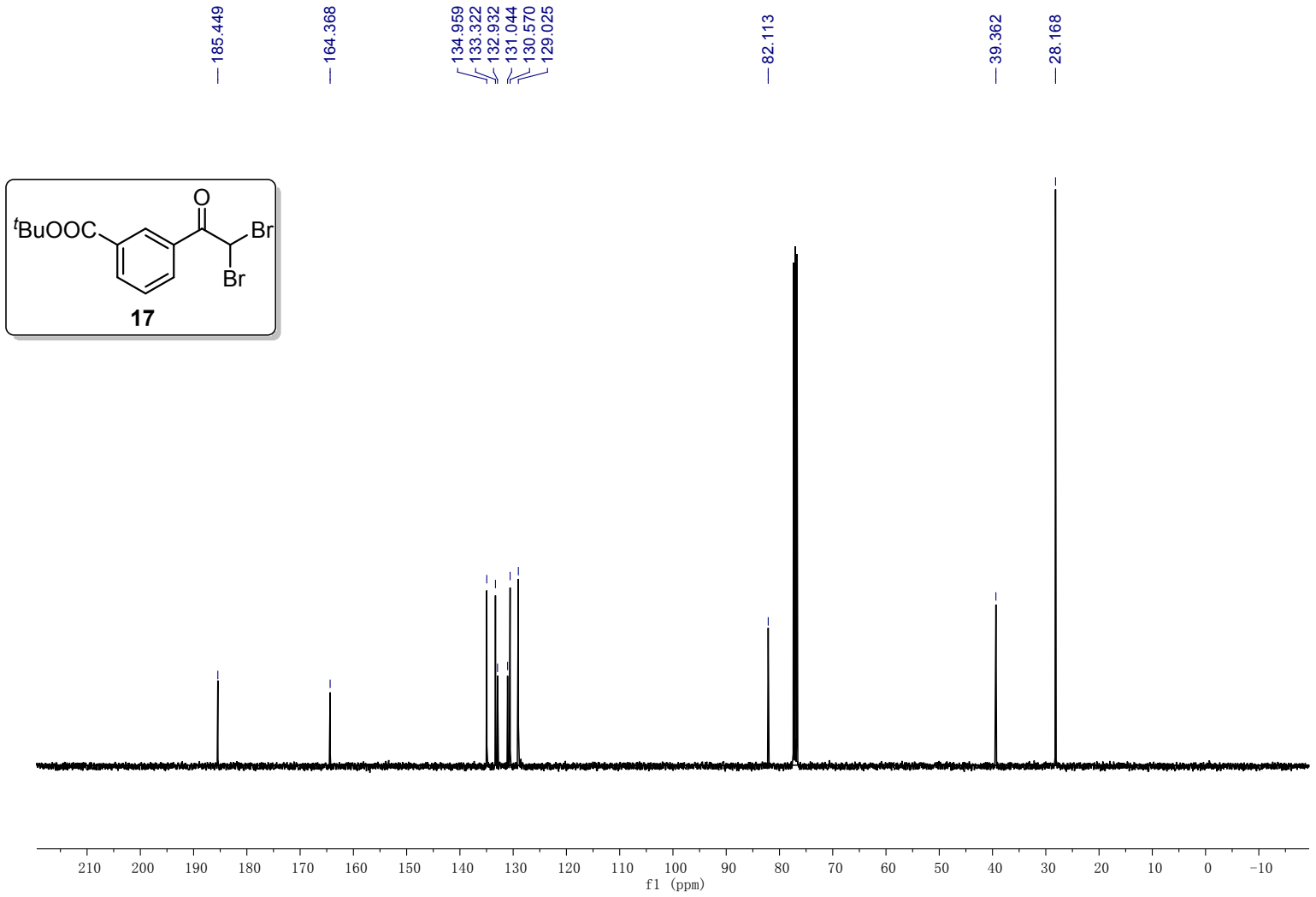
## $^{13}$C NMR of 16


185.879
160.009
132.131
129.881
121.964
121.061
114.078
55.573
39.646
MeO
O
Br
Br
16
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)

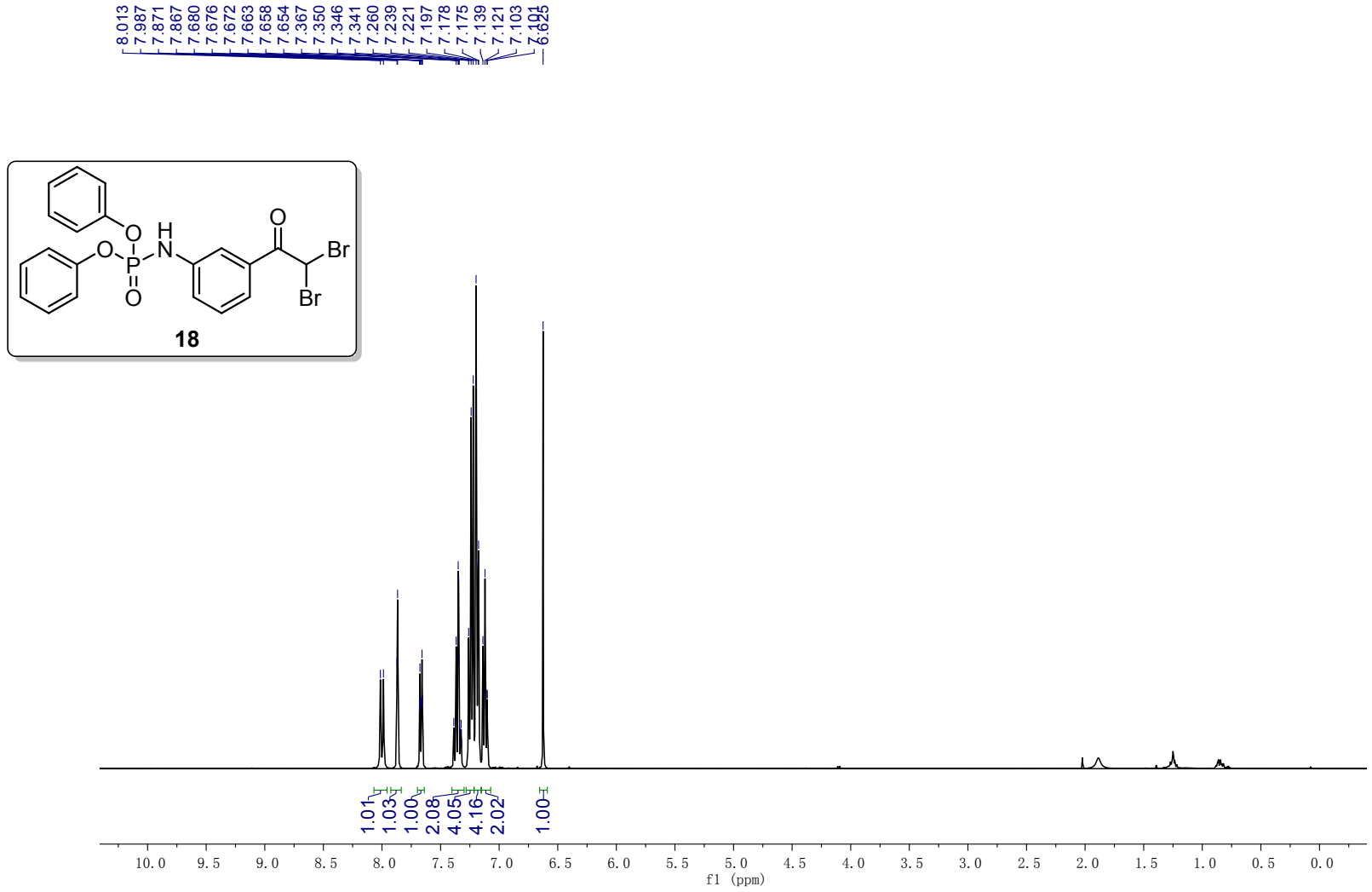
**$^1$H NMR of 17**


8.670
8.667
8.663
8.246
8.238
8.230
7.577
7.558
6.710
1.647
O
tBuOOC
Br
Br
17
0.99
1.99
1.01
1.00
9.07
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

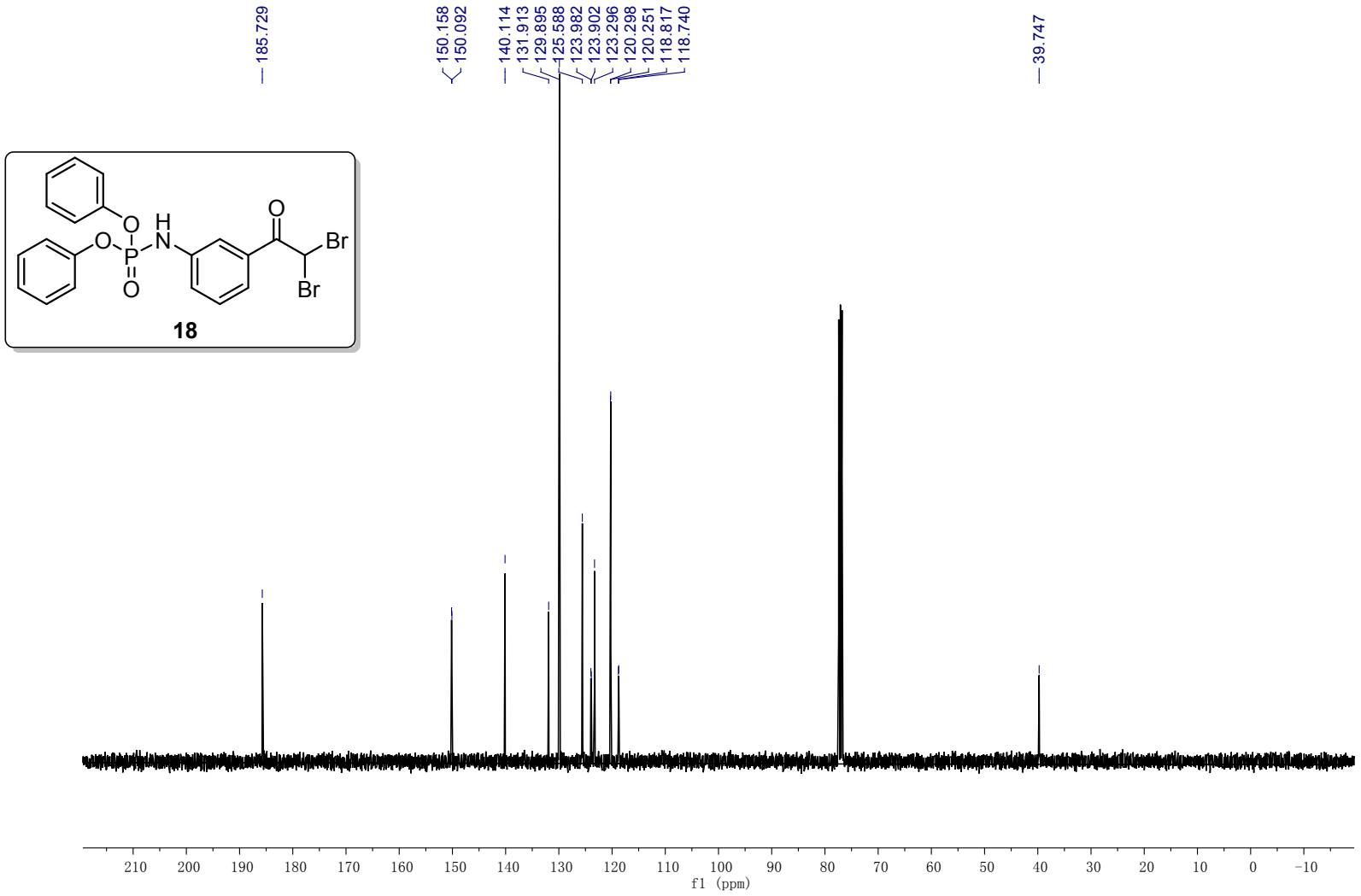
## $^{13}$C NMR of 17


185.449
164.368
134.959
133.322
132.932
131.044
130.570
129.025
82.113
39.362
28.168
tBuOOC
O
Br
Br
17
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)

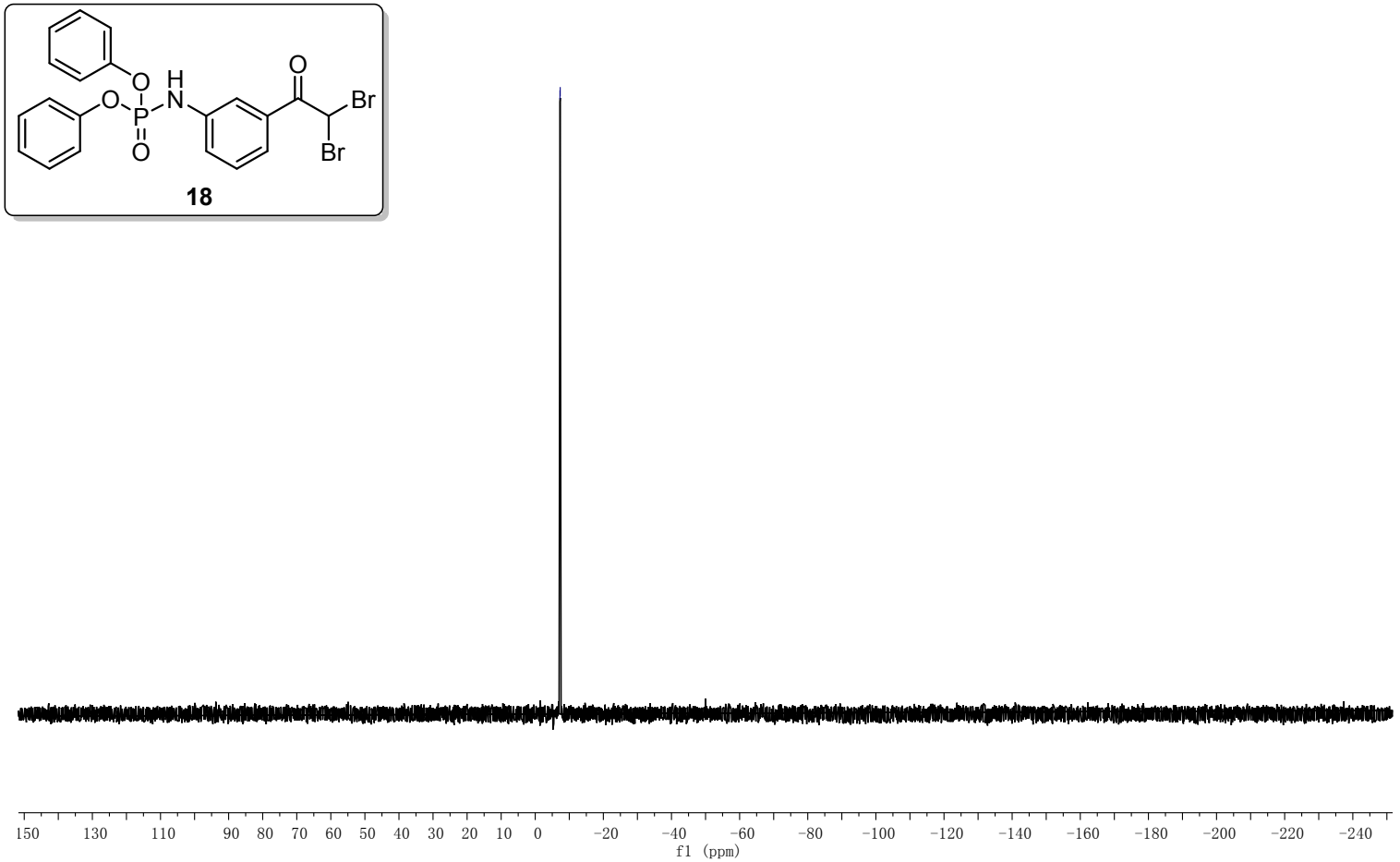
## $^{1}$H NMR of 18


8.013
7.987
7.871
7.867
7.680
7.676
7.672
7.663
7.658
7.654
7.367
7.350
7.346
7.341
7.260
7.239
7.221
7.197
7.178
7.175
7.139
7.121
7.103
7.101
6.625
O
H
N
O
O
P
O
Br
Br
18
1.01
1.03
1.00
2.08
4.05
4.16
2.02
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

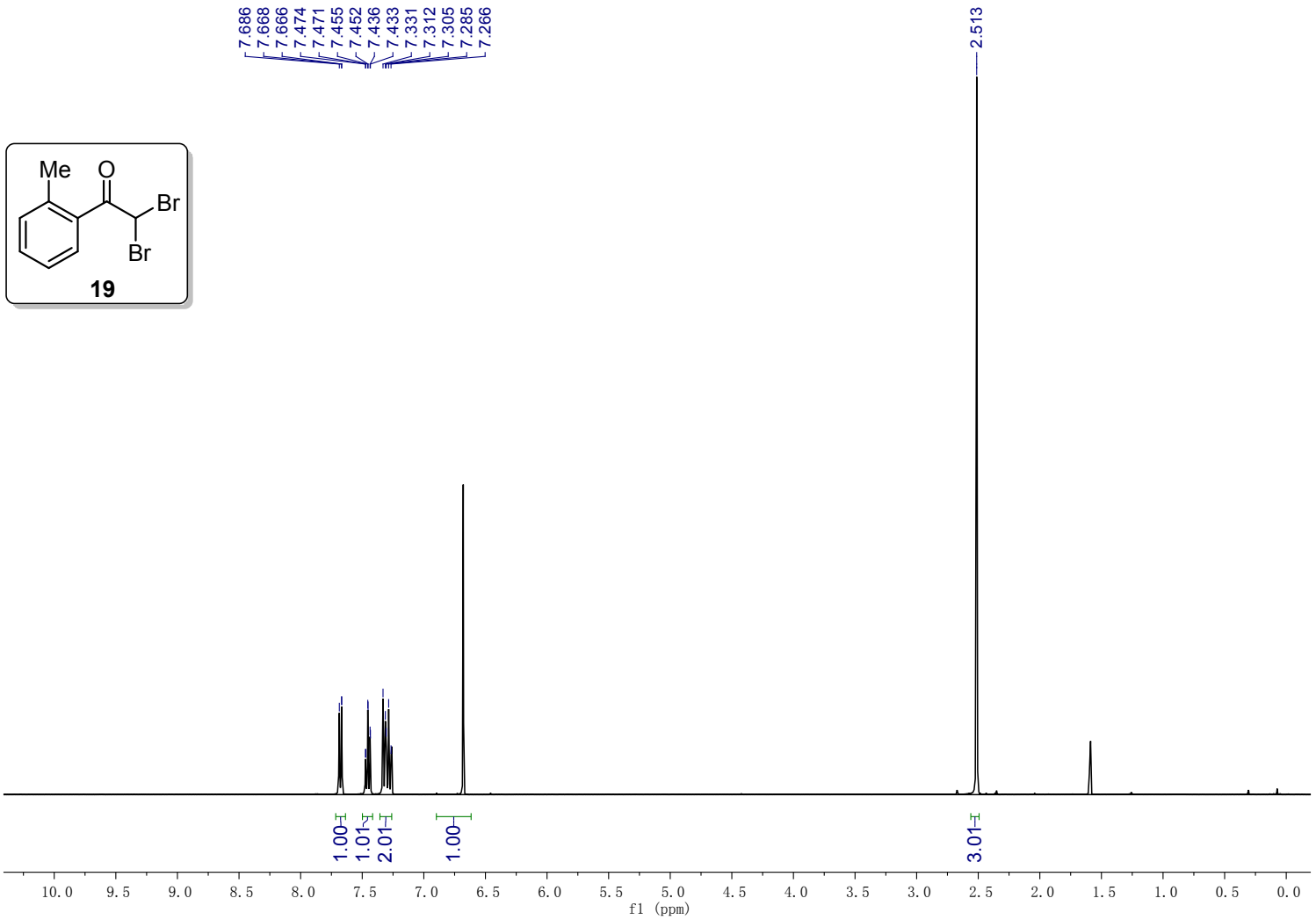
## $^{13}$C NMR of 18


185.729
150.158
150.092
140.114
131.913
129.895
125.588
123.982
123.902
123.296
120.298
120.251
118.817
118.740
39.747
O
H
N
O
O
P
O
O
Br
Br
18
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)

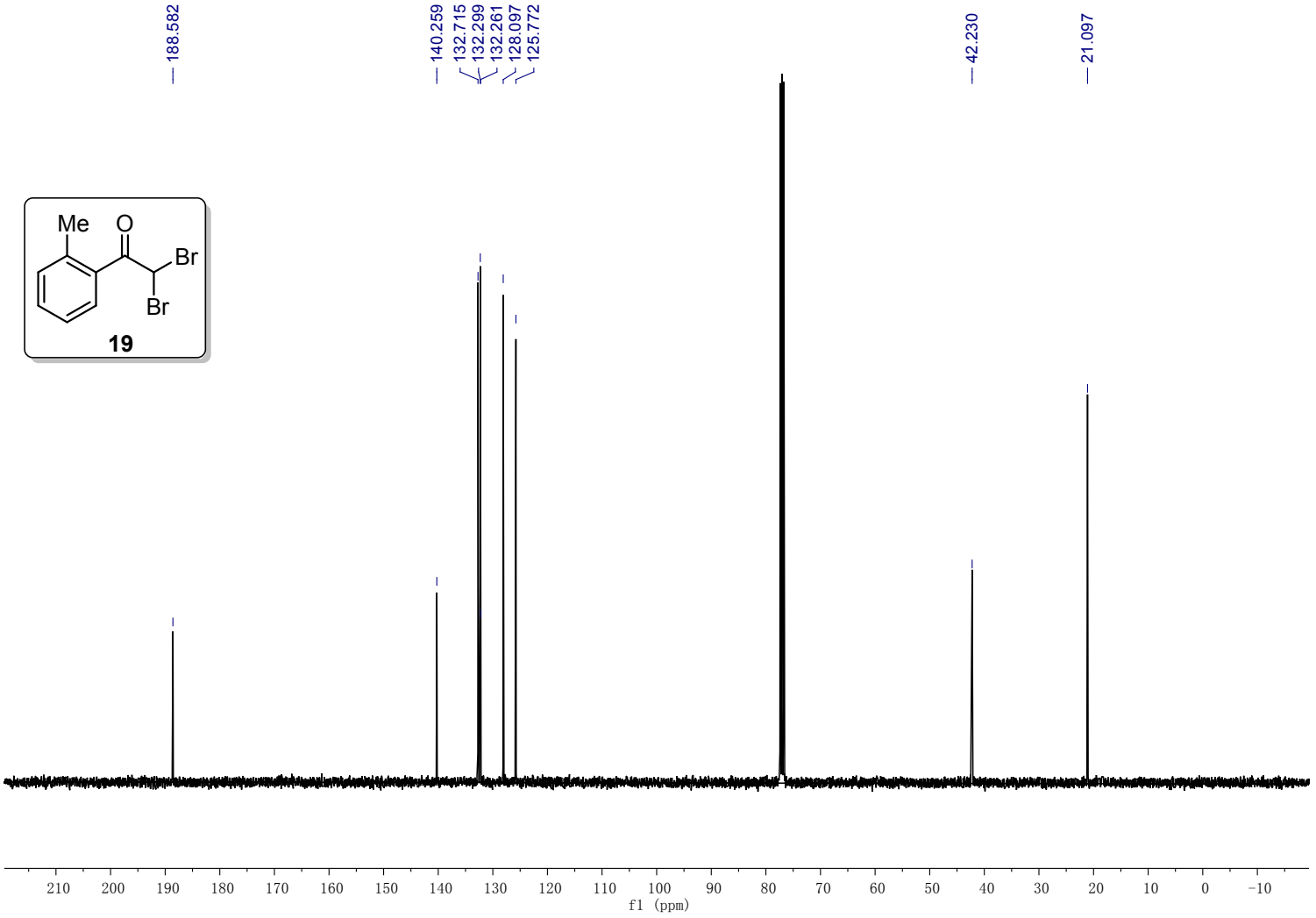
## $^{31}$P NMR of 18


-7.260
-7.340
O
H
N
O
O
P
O
O
Br
Br
18
150 130 110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

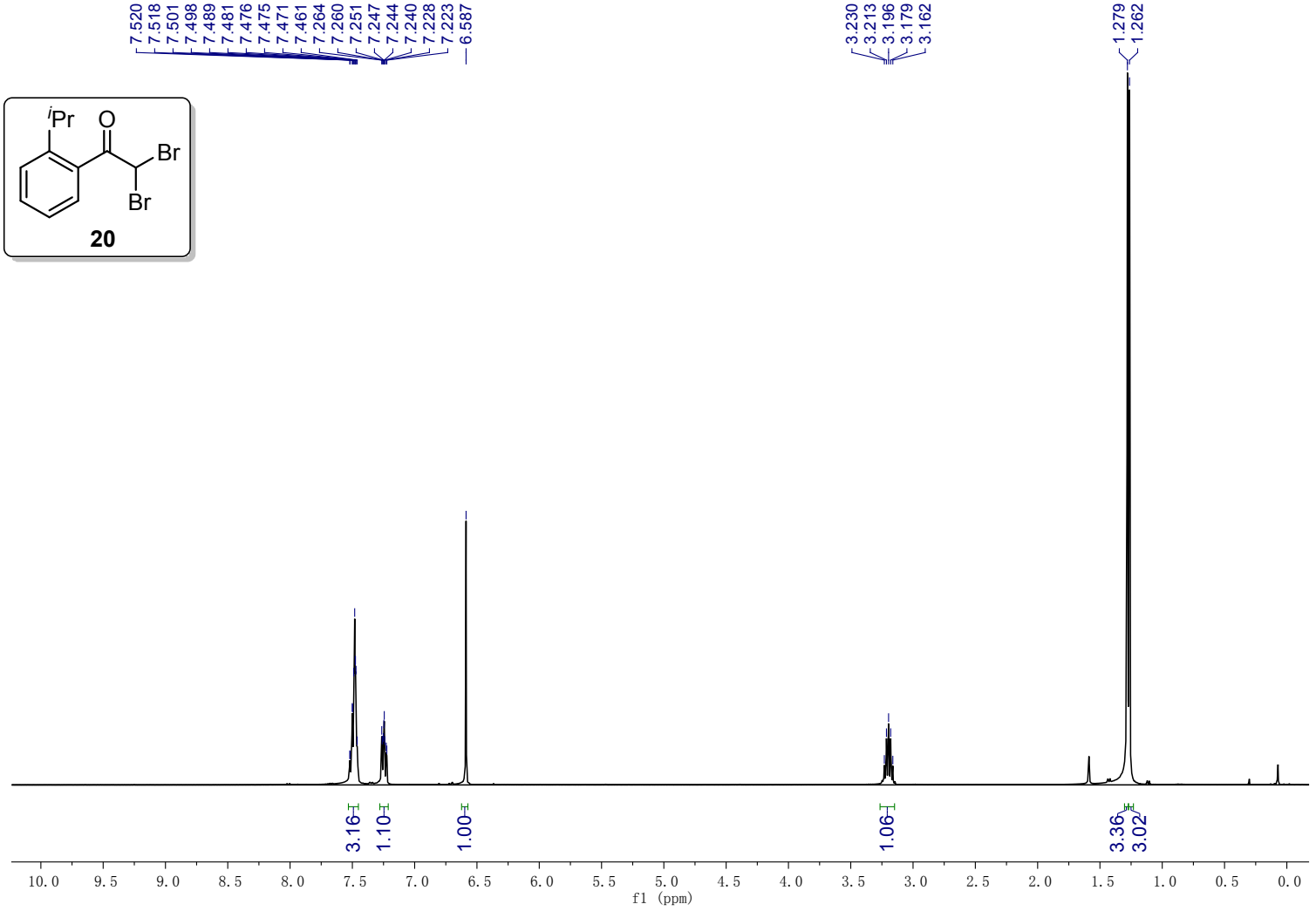
## $^{1}$H NMR of 19


7.686
7.668
7.666
7.474
7.471
7.455
7.452
7.436
7.433
7.331
7.312
7.305
7.285
7.266
2.513
Me
O
Br
Br
19
1.00
1.01
2.01
1.00
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

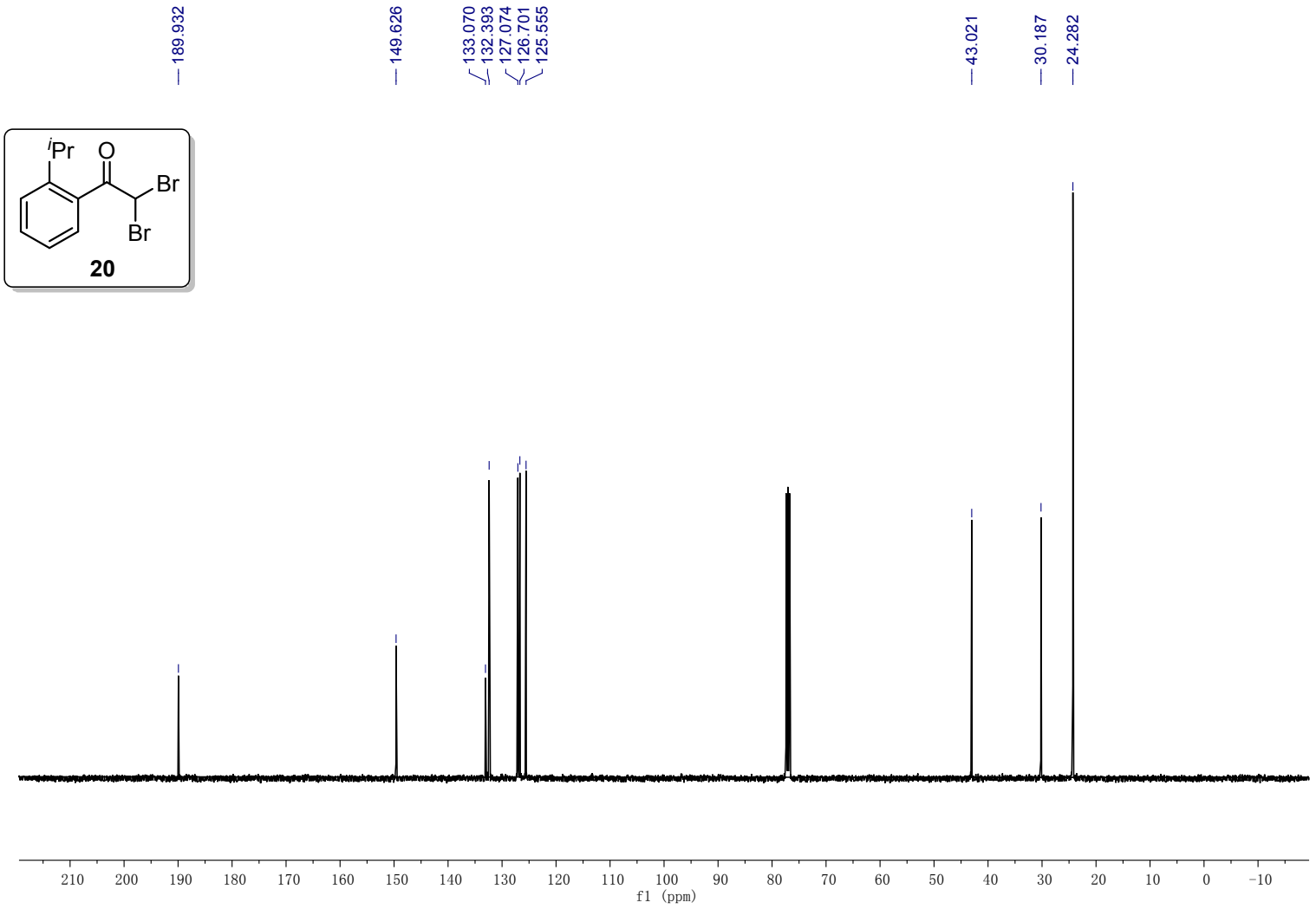
## $^{13}$C NMR of 19


188.582
140.259
132.715
132.299
132.261
128.097
125.772
42.230
21.097
Me
O
Br
Br
19
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)

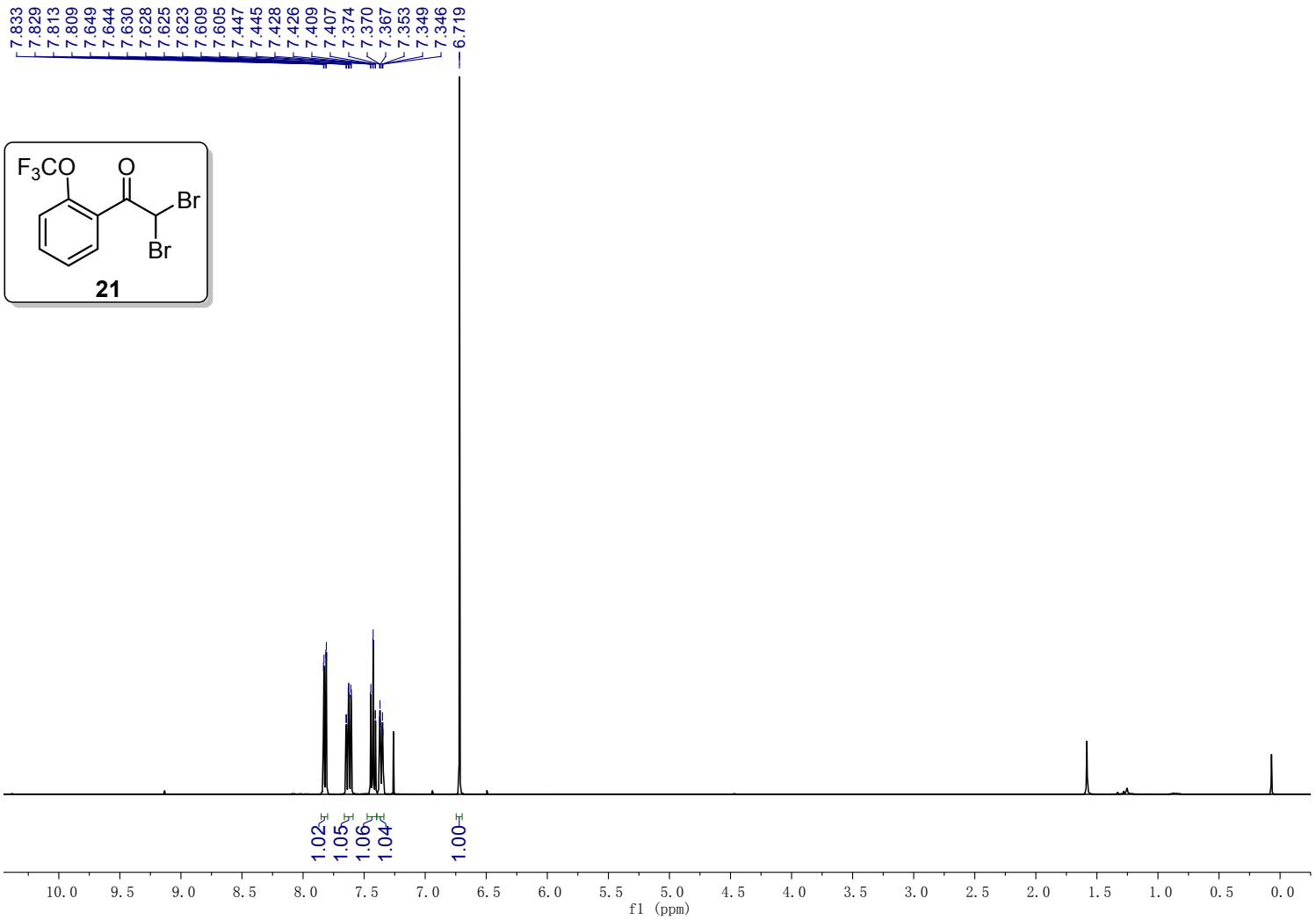
## $^1$H NMR of 20


7.520
7.518
7.501
7.498
7.489
7.481
7.476
7.475
7.471
7.461
7.264
7.260
7.251
7.247
7.244
7.240
7.228
7.223
6.587
3.230
3.213
3.196
3.179
3.162
1.279
1.262
iPr
O
Br
Br
20
3.16
1.10
1.00
1.06
3.36
3.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

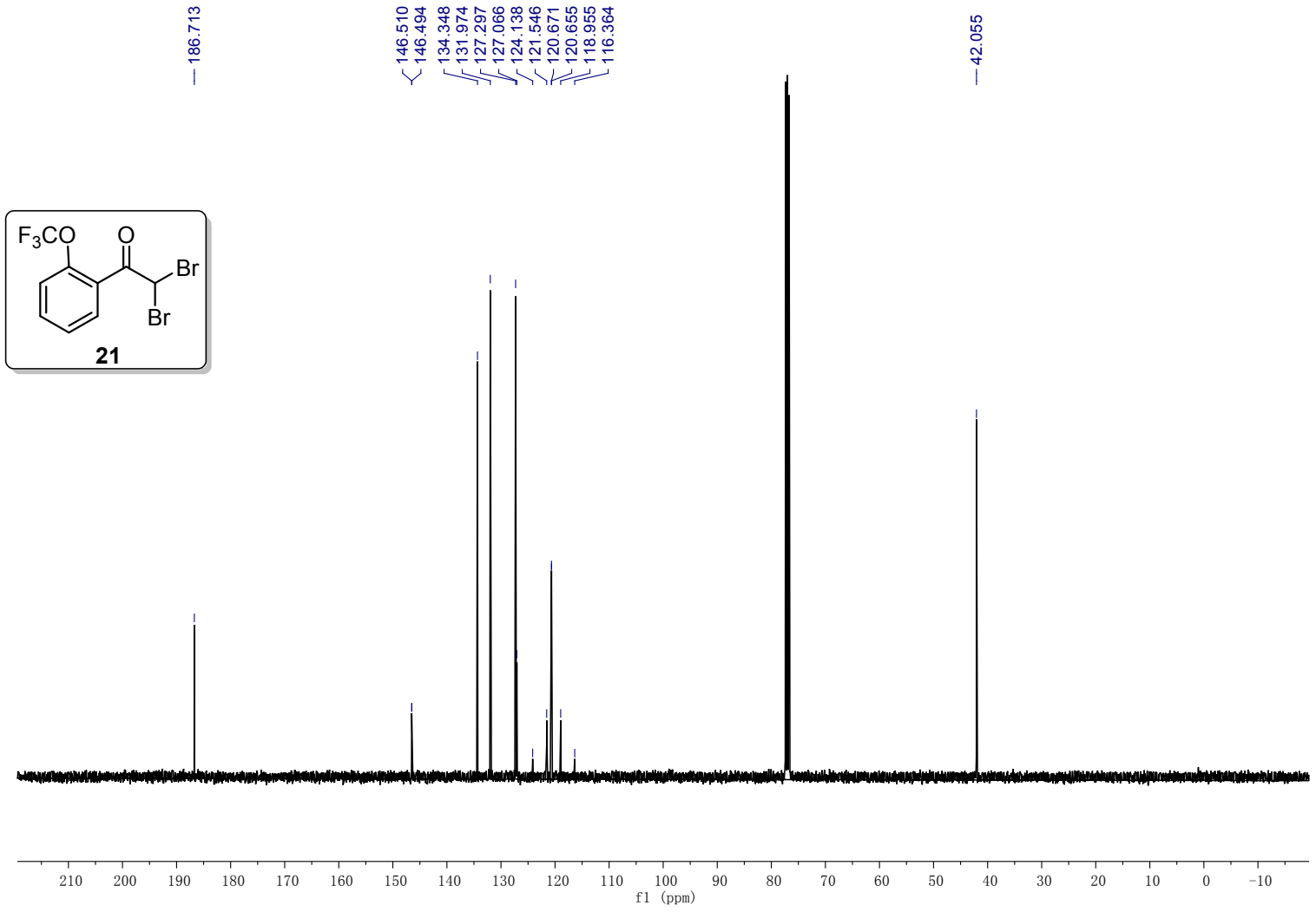
## $^{13}$C NMR of 20


189.932
149.626
133.070
132.393
127.074
126.701
125.555
43.021
30.187
24.282
iPr
O
Br
Br
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)

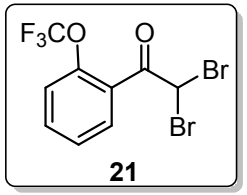
## $^{1}$H NMR of 21


7.833
7.829
7.813
7.809
7.649
7.644
7.630
7.628
7.625
7.623
7.609
7.605
7.447
7.445
7.428
7.426
7.409
7.407
7.374
7.370
7.367
7.353
7.349
7.346
6.719
F3CO
O
Br
Br
21
1.02
1.05
1.06
1.04
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

## $^{13}$C NMR of 21

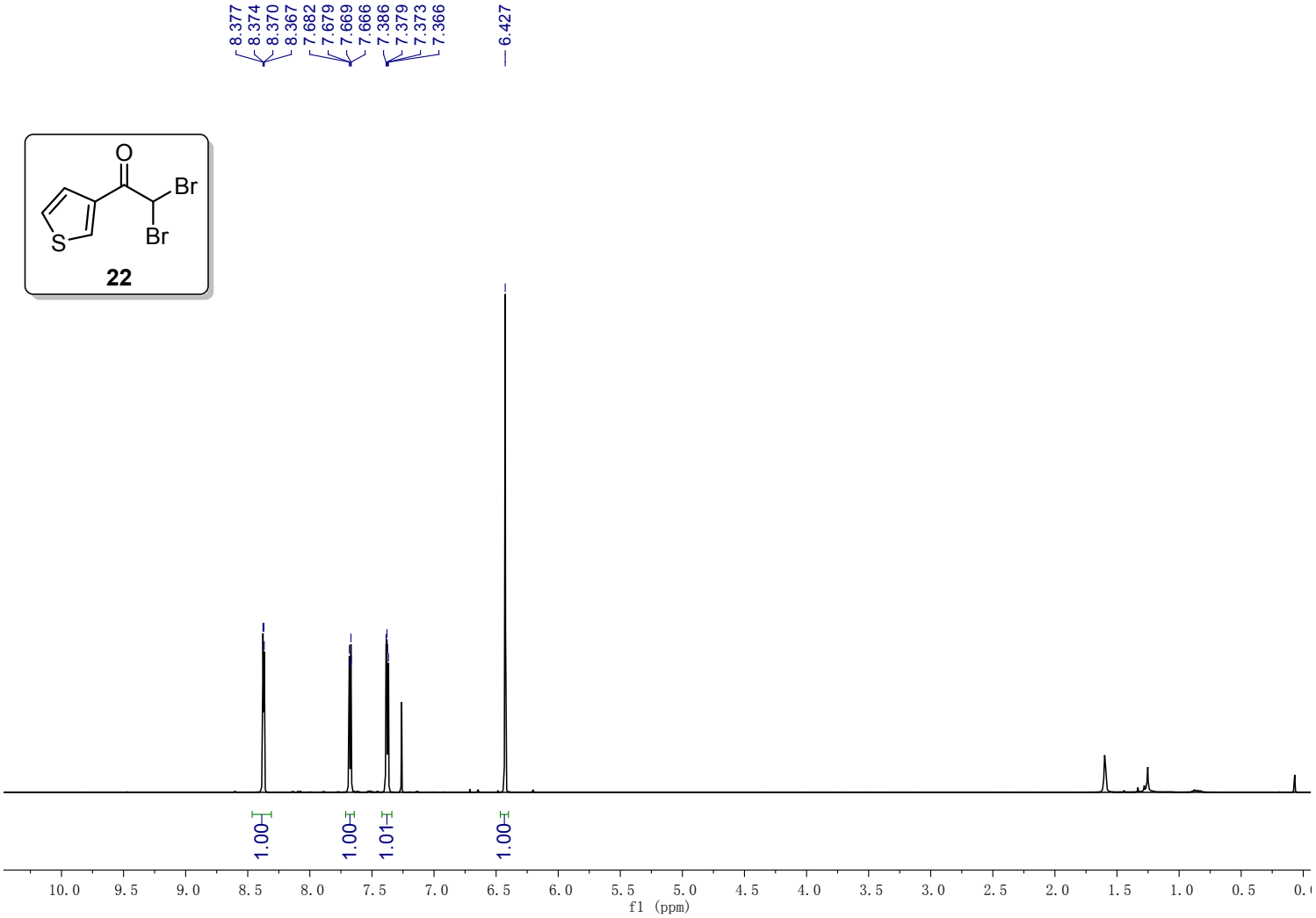

186.713
146.510
146.494
134.348
131.974
127.297
127.066
124.138
121.546
120.671
120.655
118.955
116.364
42.055
F3CO
O
Br
Br
21
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

## $^{19}$F NMR of 21

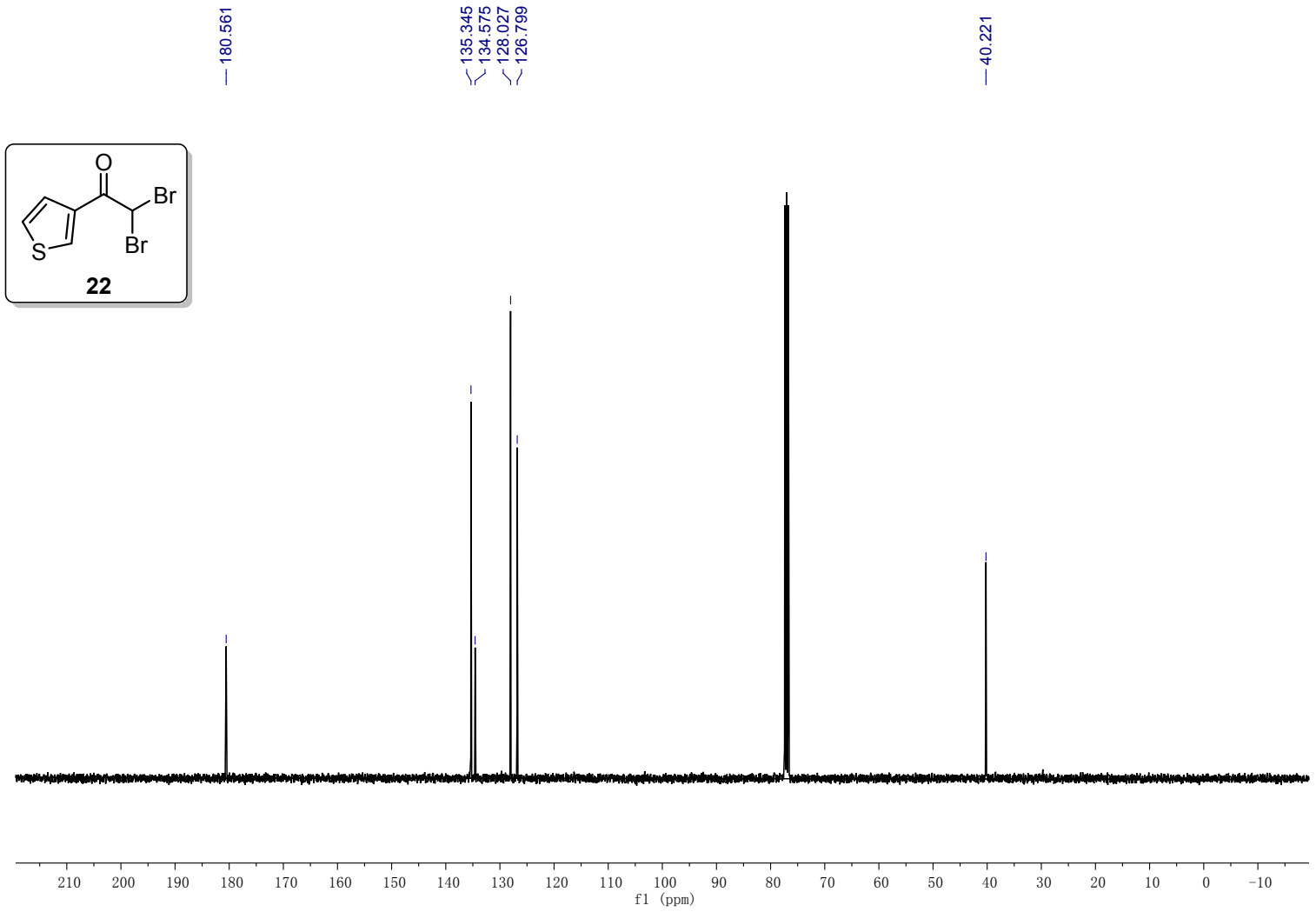



**21**

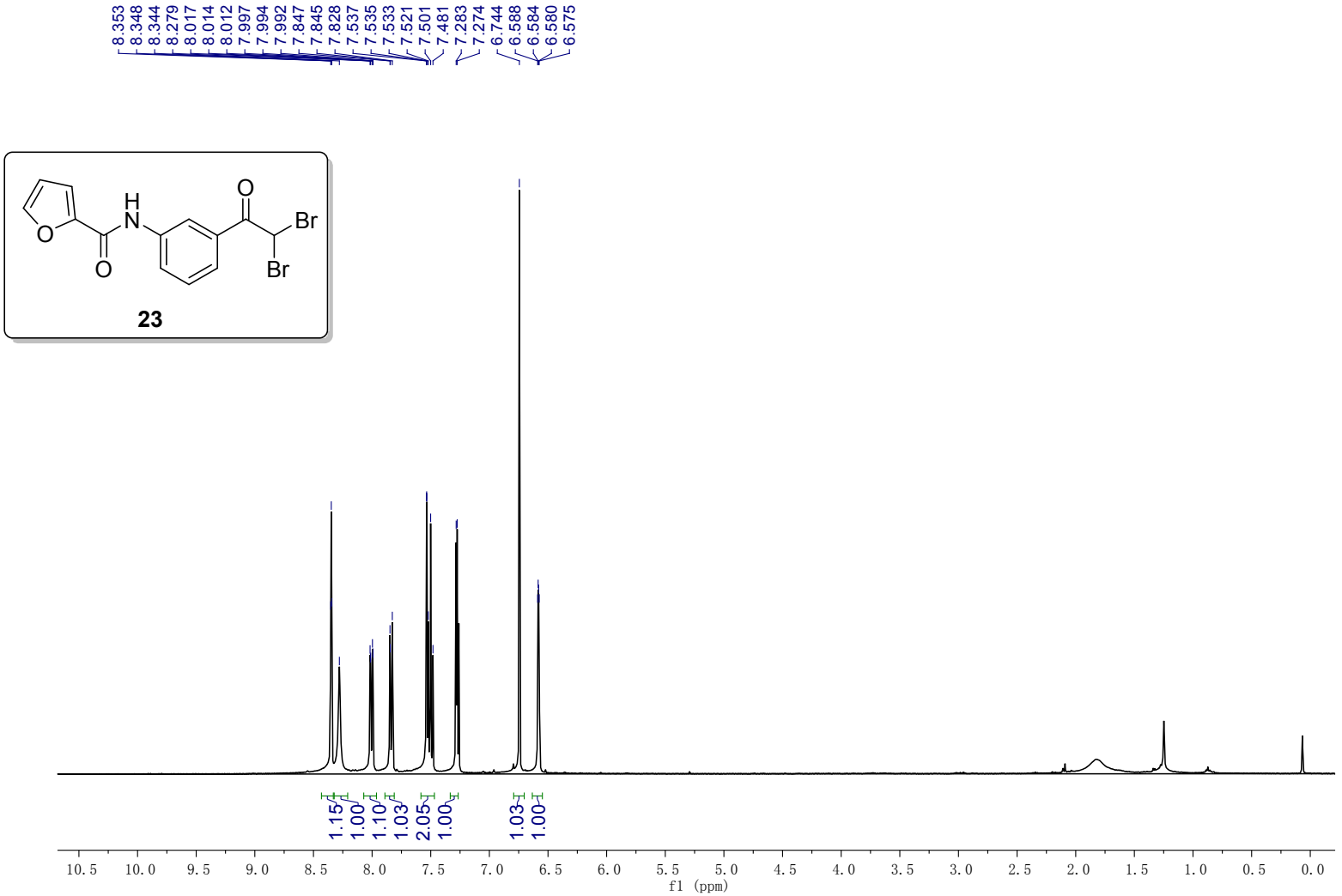
**$^1$H NMR of 22**


8.377
8.374
8.370
8.367
7.682
7.679
7.669
7.666
7.386
7.379
7.373
7.366
6.427
O
Br
Br
S
22
1.00
1.00
1.01
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

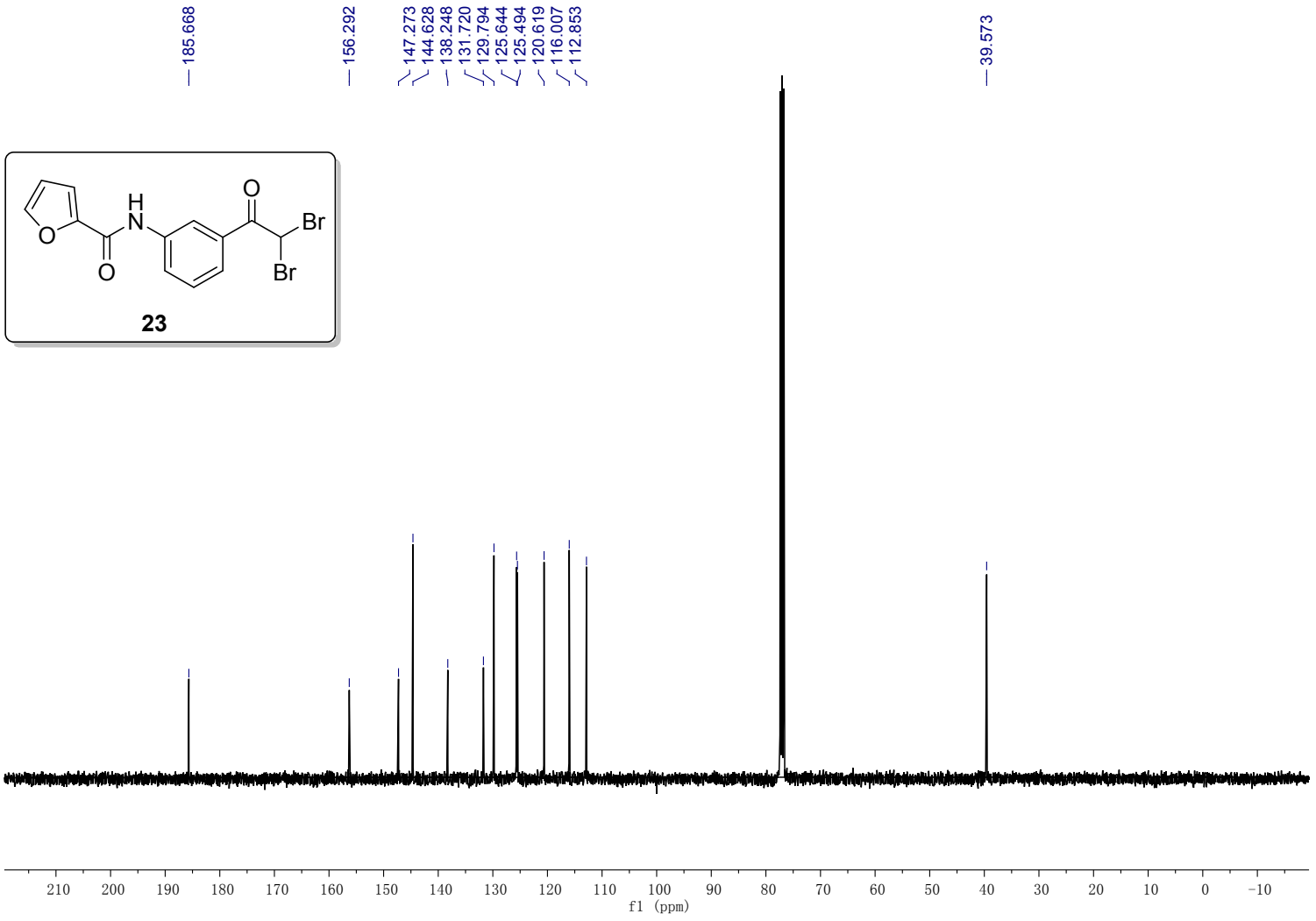
## $^{13}$C NMR of 22


180.561
135.345
134.575
128.027
126.799
40.221
O
Br
Br
S
22
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)

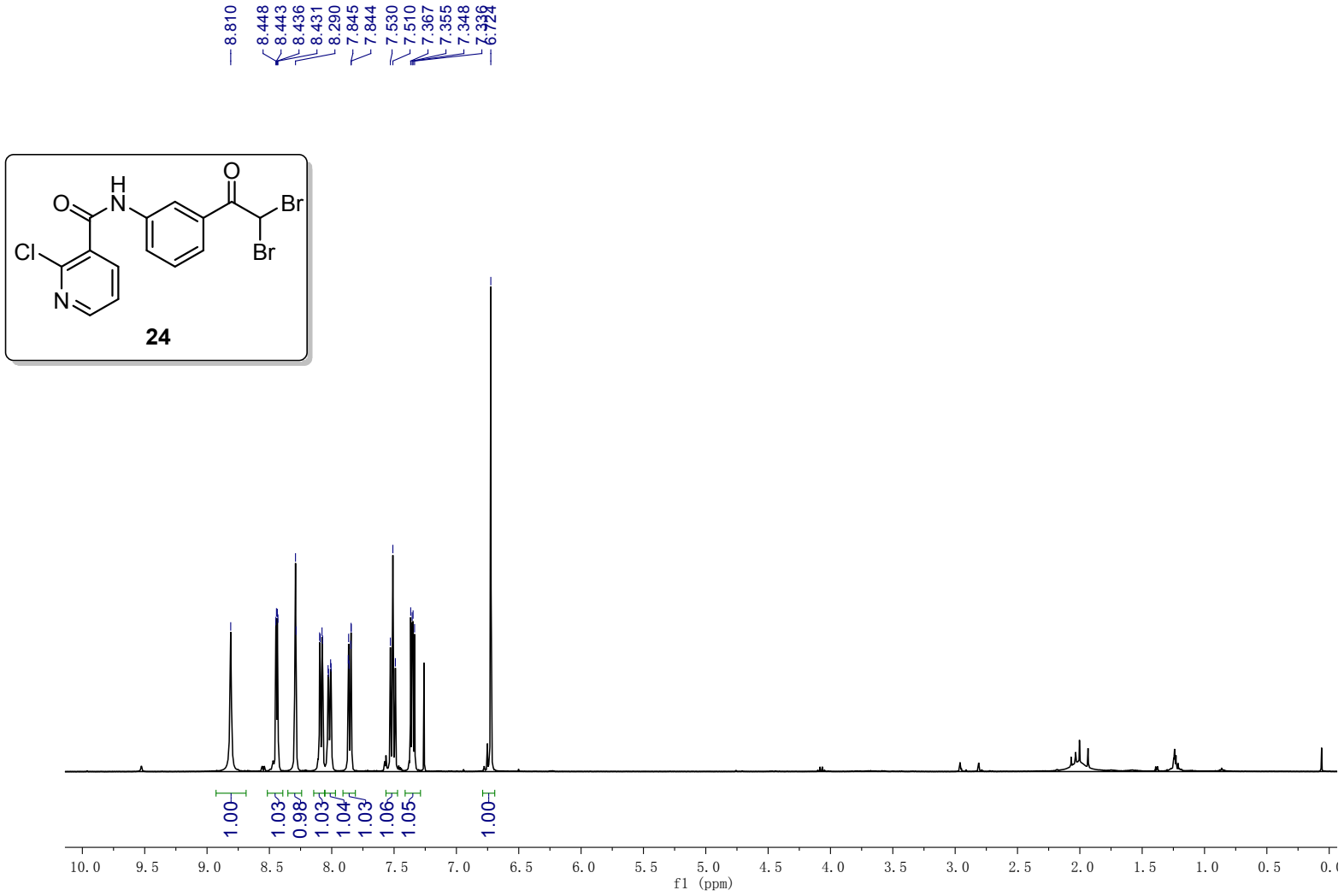
## $^{1}$H NMR of 23


8.353
8.348
8.344
8.279
8.017
8.014
8.012
7.997
7.994
7.992
7.847
7.845
7.828
7.537
7.535
7.533
7.521
7.501
7.481
7.283
7.274
6.744
6.588
6.584
6.580
6.575
H
N
O
O
O
Br
Br
23
1.15
1.00
1.10
1.03
2.05
1.00
1.03
1.00
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
f1 (ppm)

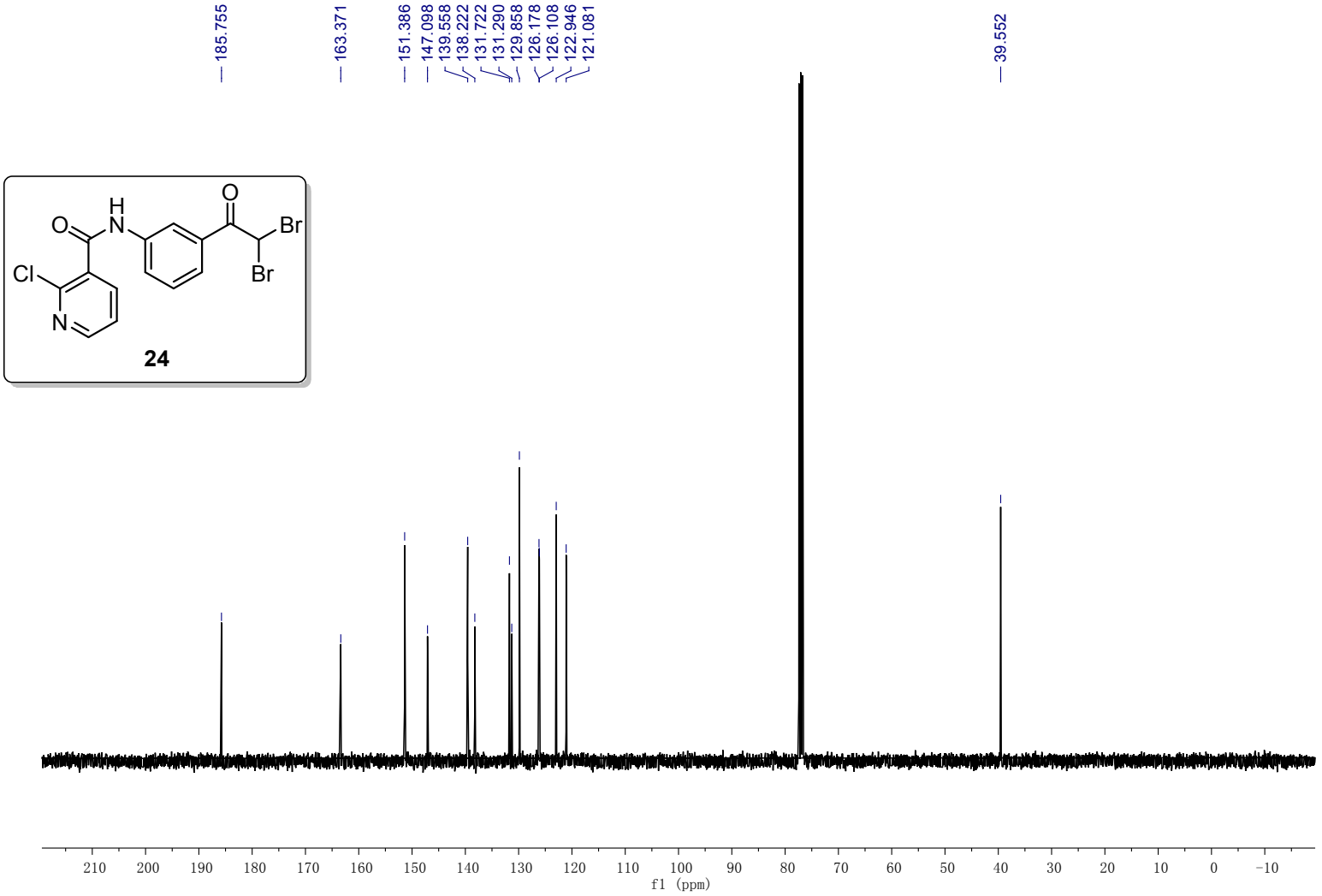
## $^{13}$C NMR of 23


185.668
156.292
147.273
144.628
138.248
131.720
129.794
125.644
125.494
120.619
116.007
112.853
39.573
H
N
O
O
O
Br
Br
23
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)

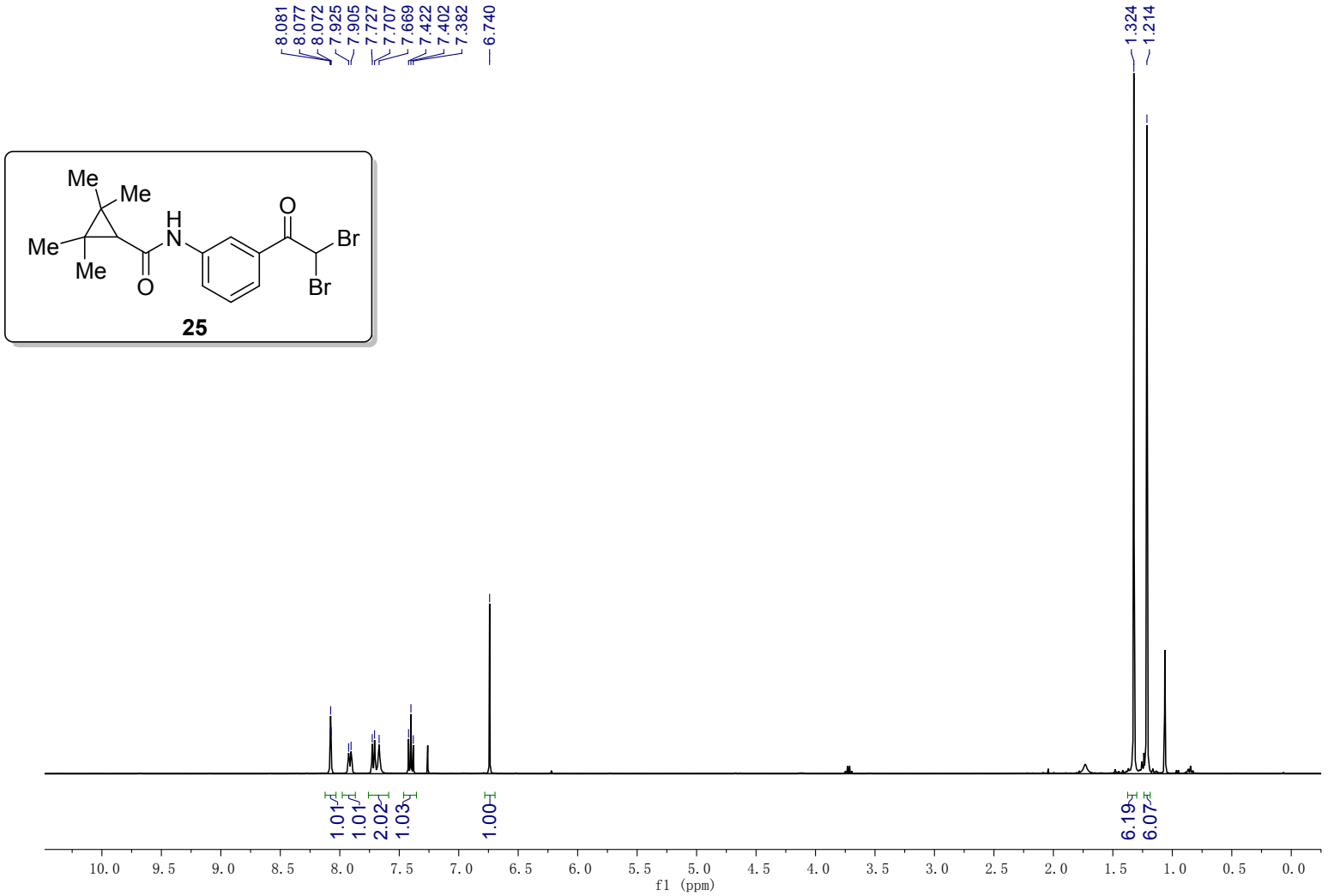
## $^{1}$H NMR of 24


8.810
8.448
8.443
8.436
8.431
8.290
7.845
7.844
7.530
7.510
7.367
7.355
7.348
7.336
7.324
O
H
N
O
Br
Br
Cl
N
24
1.00
1.03
0.98
1.03
1.04
1.03
1.06
1.05
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

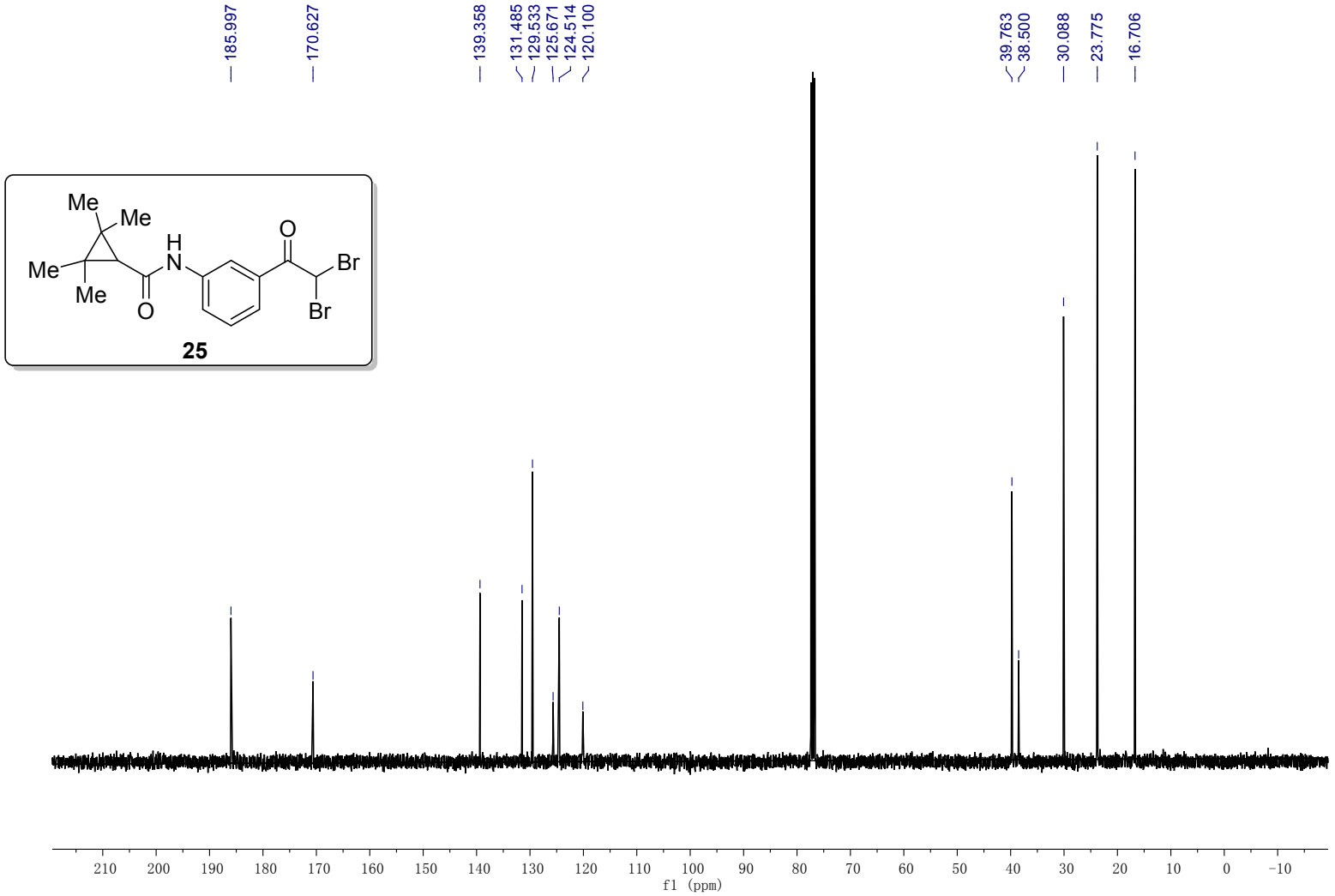
## $^{13}$C NMR of 24


185.755
163.371
151.386
147.098
139.558
138.222
131.722
131.290
129.858
126.178
126.108
122.946
121.081
39.552
O
H
N
O
Br
Br
Cl
N
24
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)

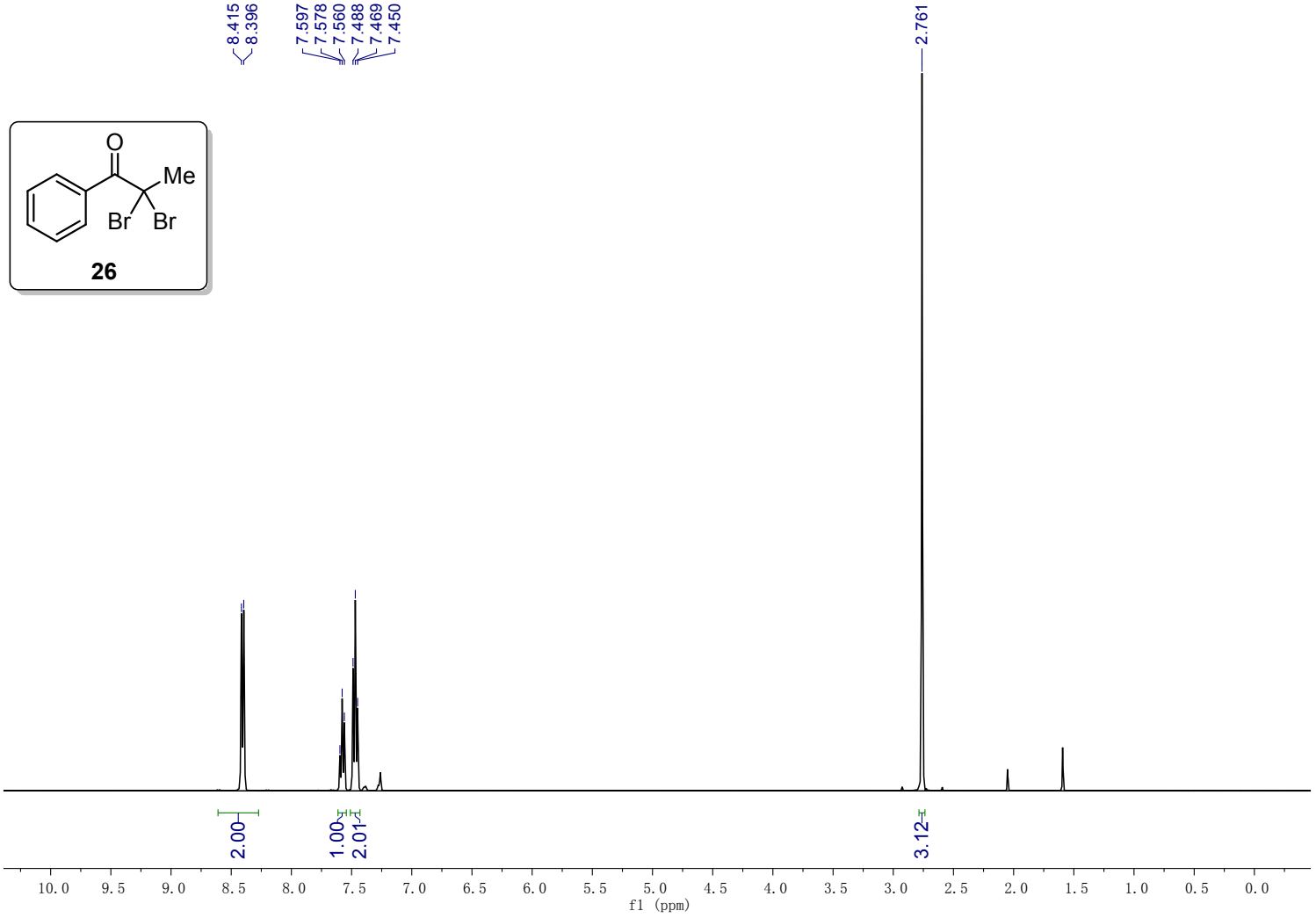
## $^{1}$H NMR of 25


8.081
8.077
8.072
7.925
7.905
7.727
7.707
7.669
7.422
7.402
7.382
6.740
1.324
1.214
Me
Me
Me
Me
H
N
O
O
Br
Br
25
1.01
1.01
2.02
1.03
1.00
6.19
6.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

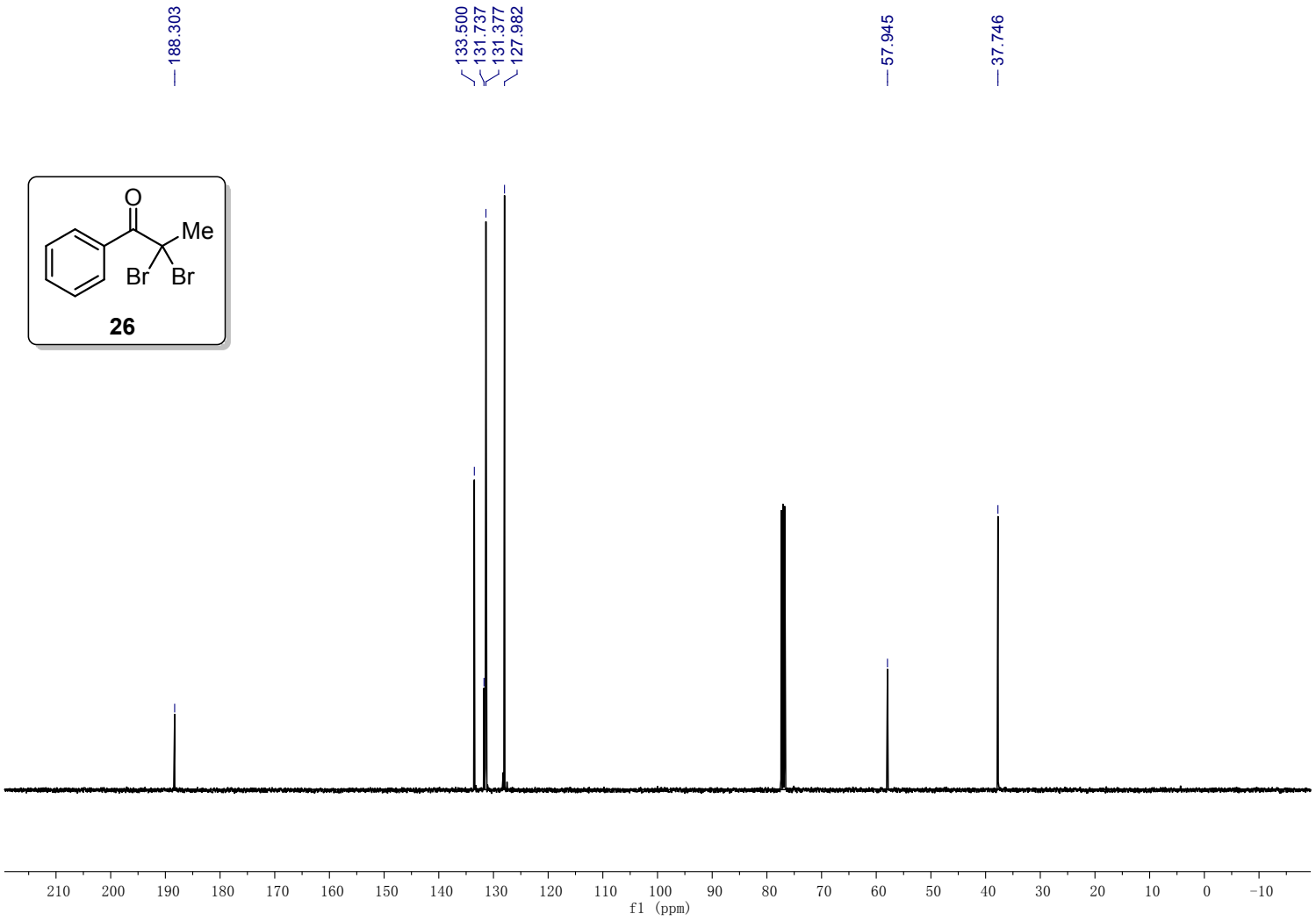
## $^{13}$C NMR of 25


185.997
170.627
139.358
131.485
129.533
125.671
124.514
120.100
39.763
38.500
30.088
23.775
16.706
Me
Me
Me
Me
H
N
O
O
Br
Br
25
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)

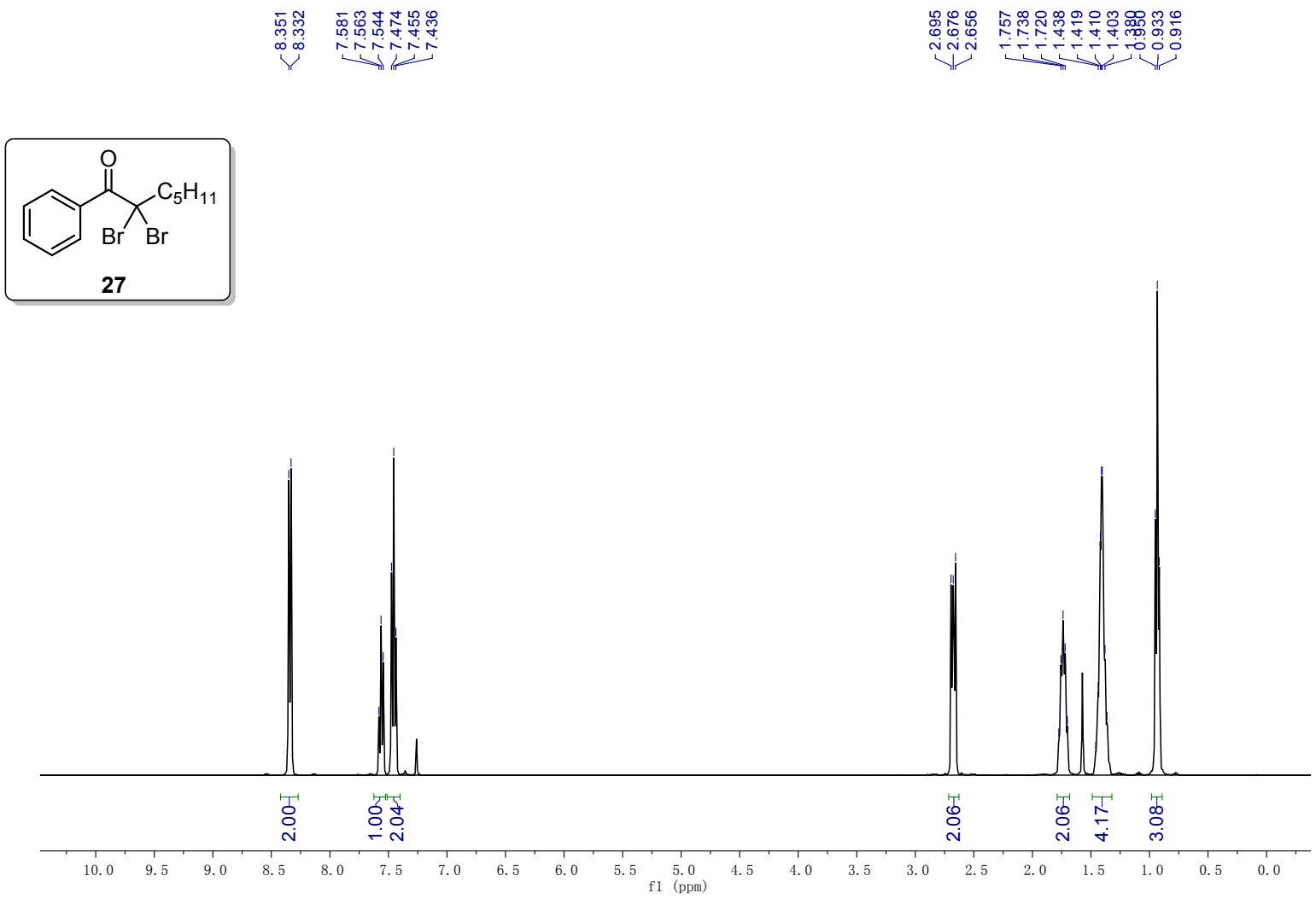
## $^{1}$HNMR of 26


8.415
8.396
7.597
7.578
7.560
7.488
7.469
7.450
2.761
O
Me
Br
Br
26
2.00
1.00
2.01
3.12
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

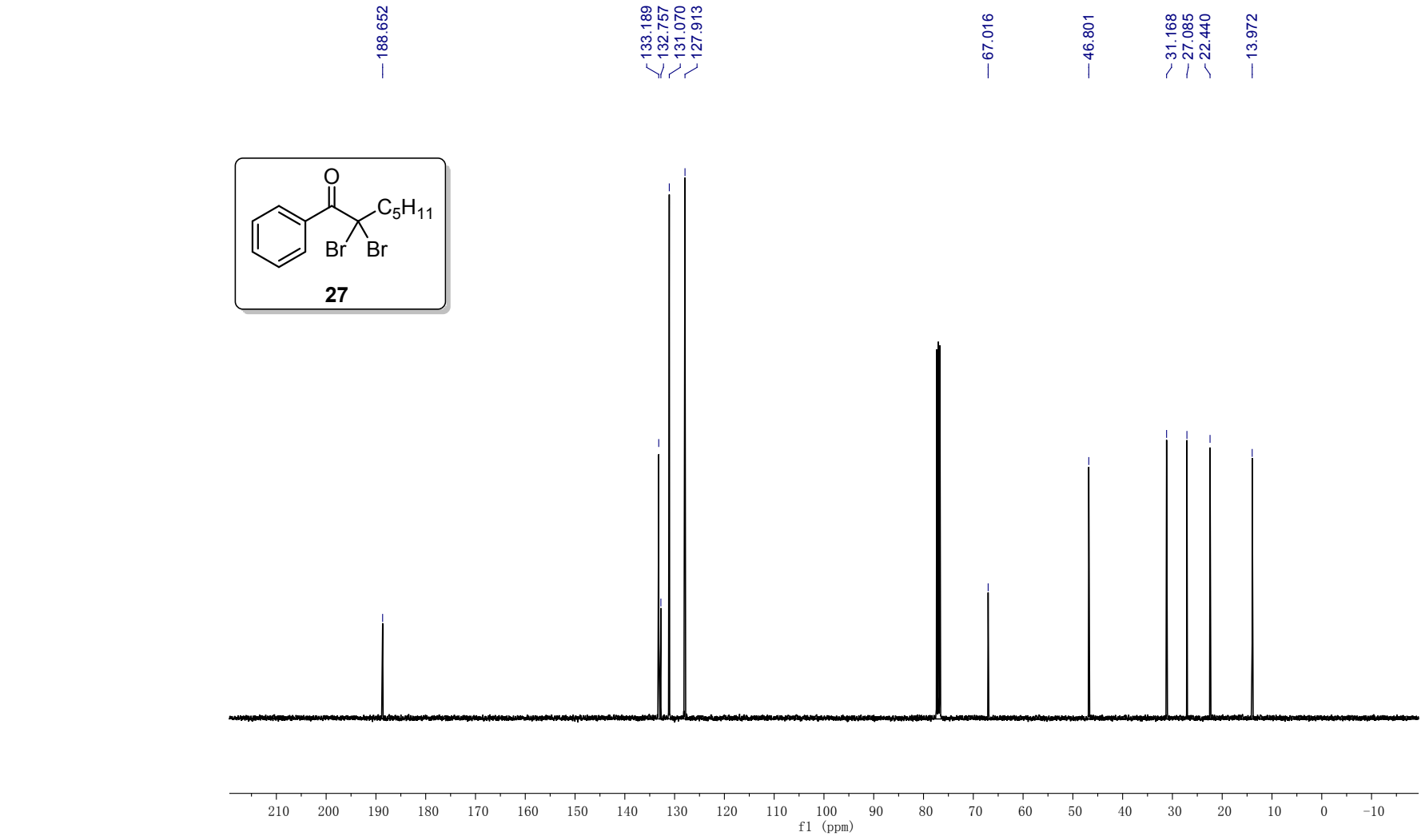
## $^{13}$C NMR of 26


188.303
133.500
131.737
131.377
127.982
57.945
37.746
O
Me
Br
Br
26
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)

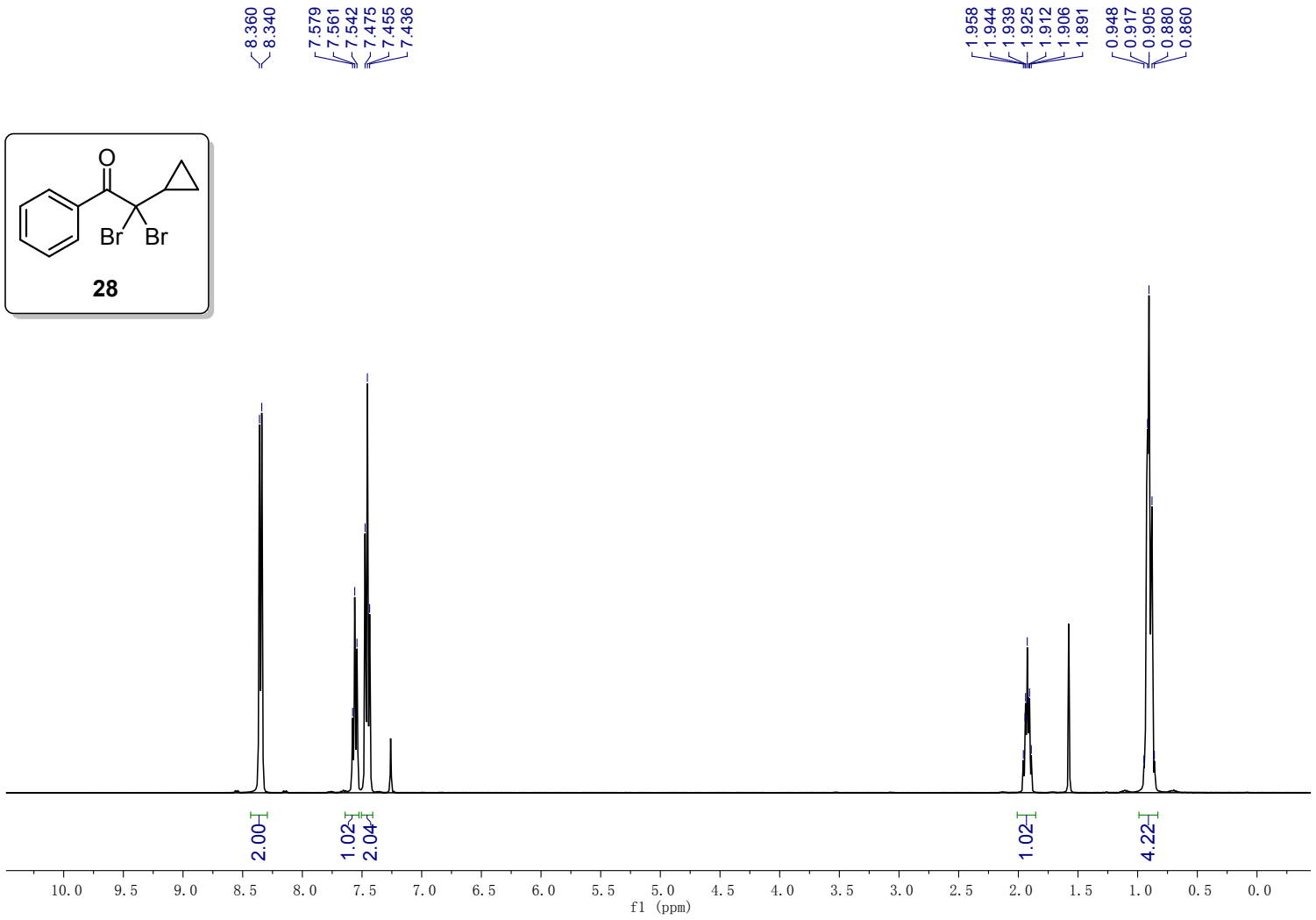
## $^{1}$H NMR of 27


8.351
8.332
7.581
7.563
7.544
7.474
7.455
7.436
2.695
2.676
2.656
1.757
1.738
1.720
1.438
1.419
1.410
1.403
0.933
0.916
O
C5H11
Br
Br
27
2.00
1.00
2.04
2.06
2.06
4.17
3.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

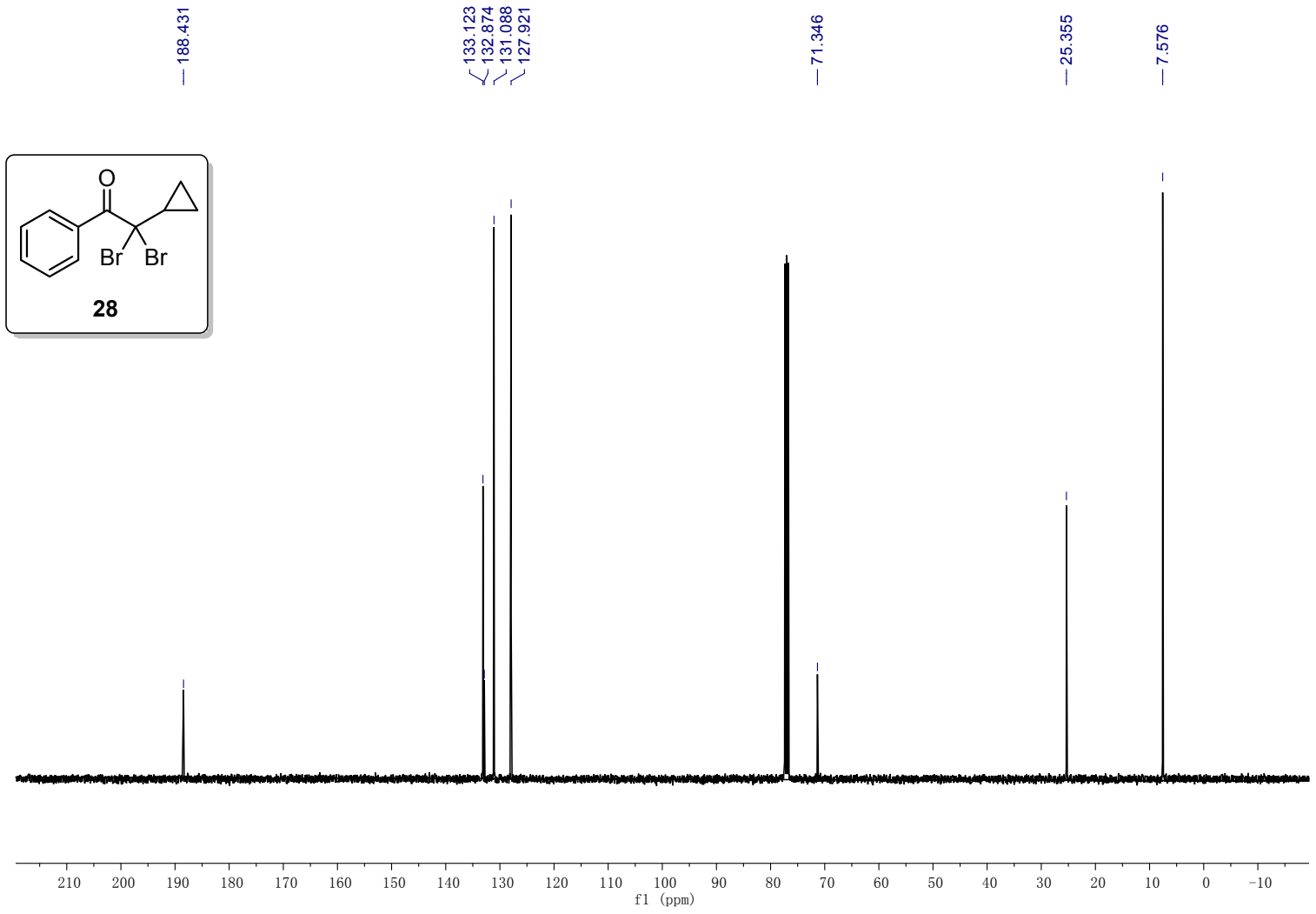
## $^{13}$C NMR of 27


188.652
133.189
132.757
131.070
127.913
67.016
46.801
31.168
27.085
22.440
13.972
O
C5H11
Br
Br
27
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)

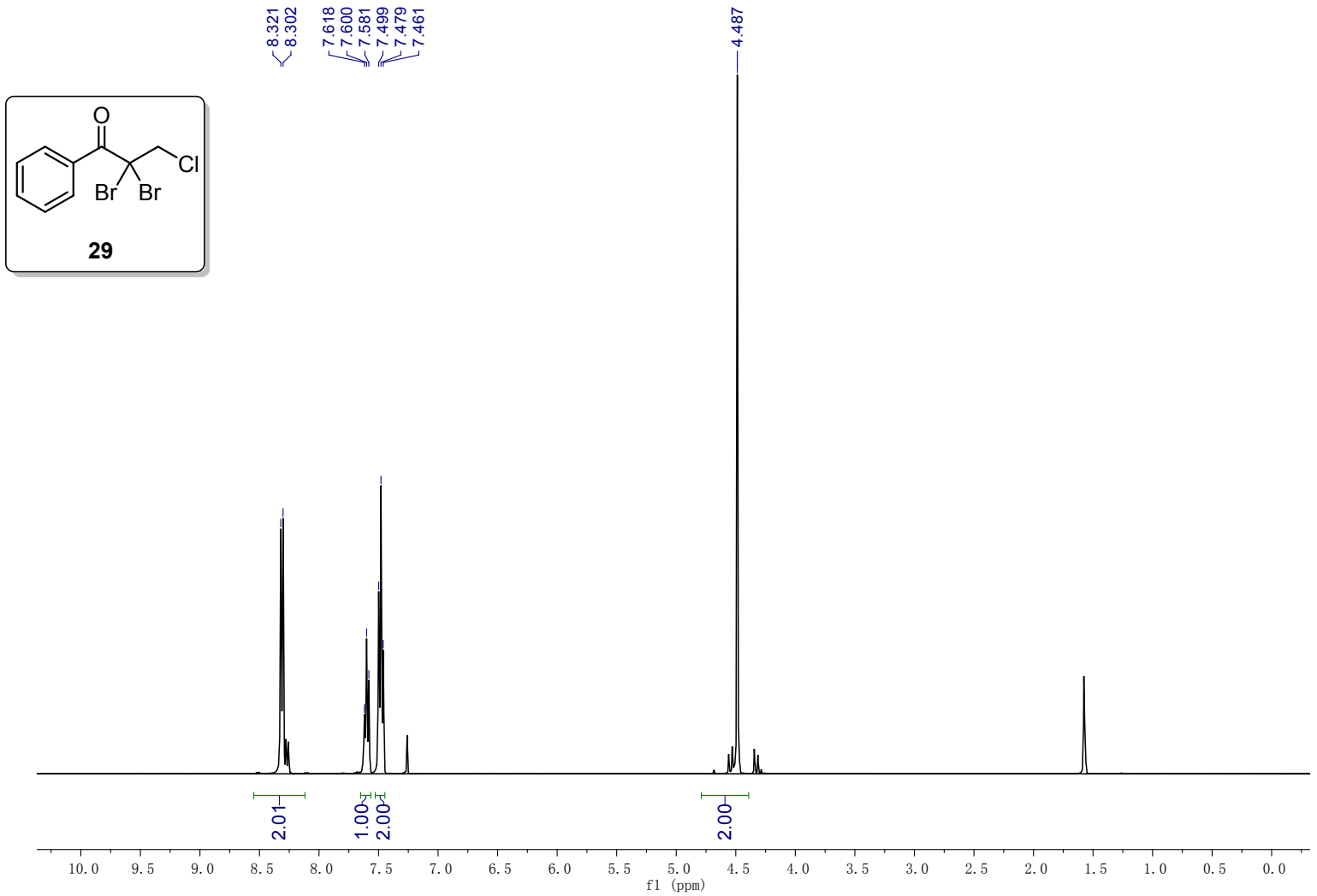
## $^{1}$H NMR of 28


8.360
8.340
7.579
7.561
7.542
7.475
7.455
7.436
1.958
1.944
1.939
1.925
1.912
1.906
1.891
0.948
0.917
0.905
0.880
0.860
O
Br
Br
28
2.00
1.02
2.04
1.02
4.22
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

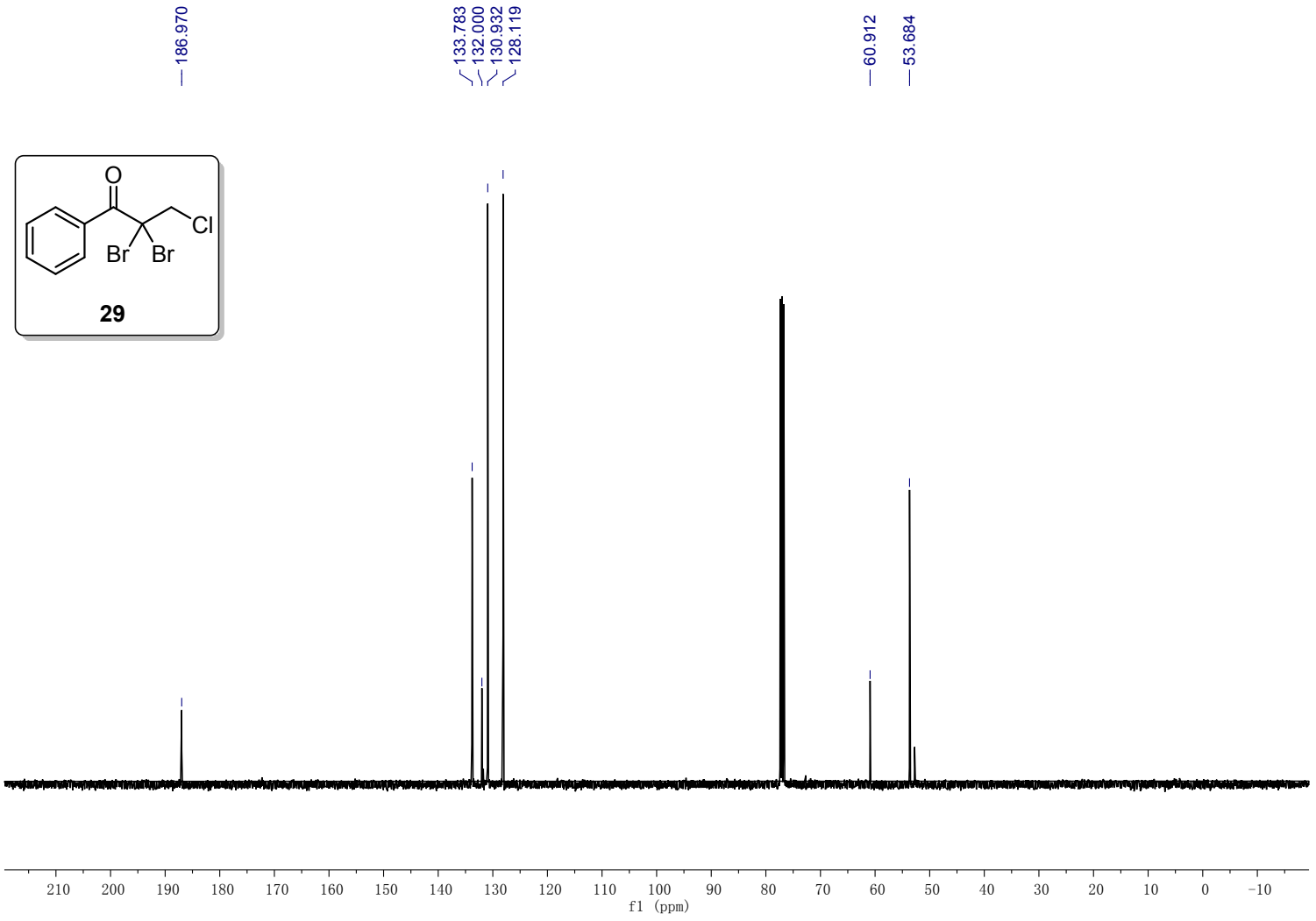
## $^{13}$C NMR of 28


188.431
133.123
132.874
131.088
127.921
71.346
25.355
7.576
O
Br
Br
28
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)

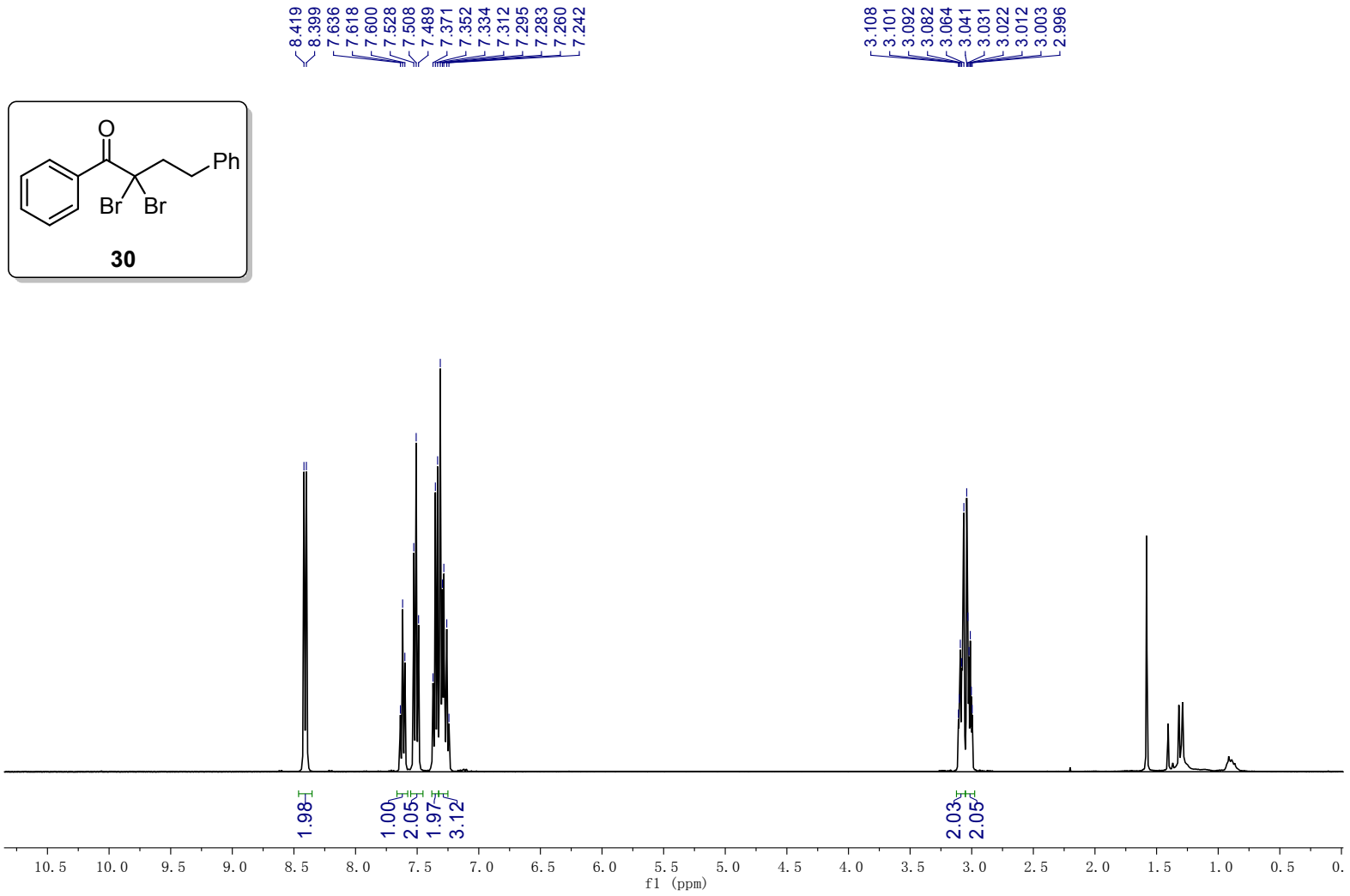
## $^{1}$H NMR of 29


8.321
8.302
7.618
7.600
7.581
7.499
7.479
7.461
4.487
O
Cl
Br
Br
29
2.01
1.00
2.00
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

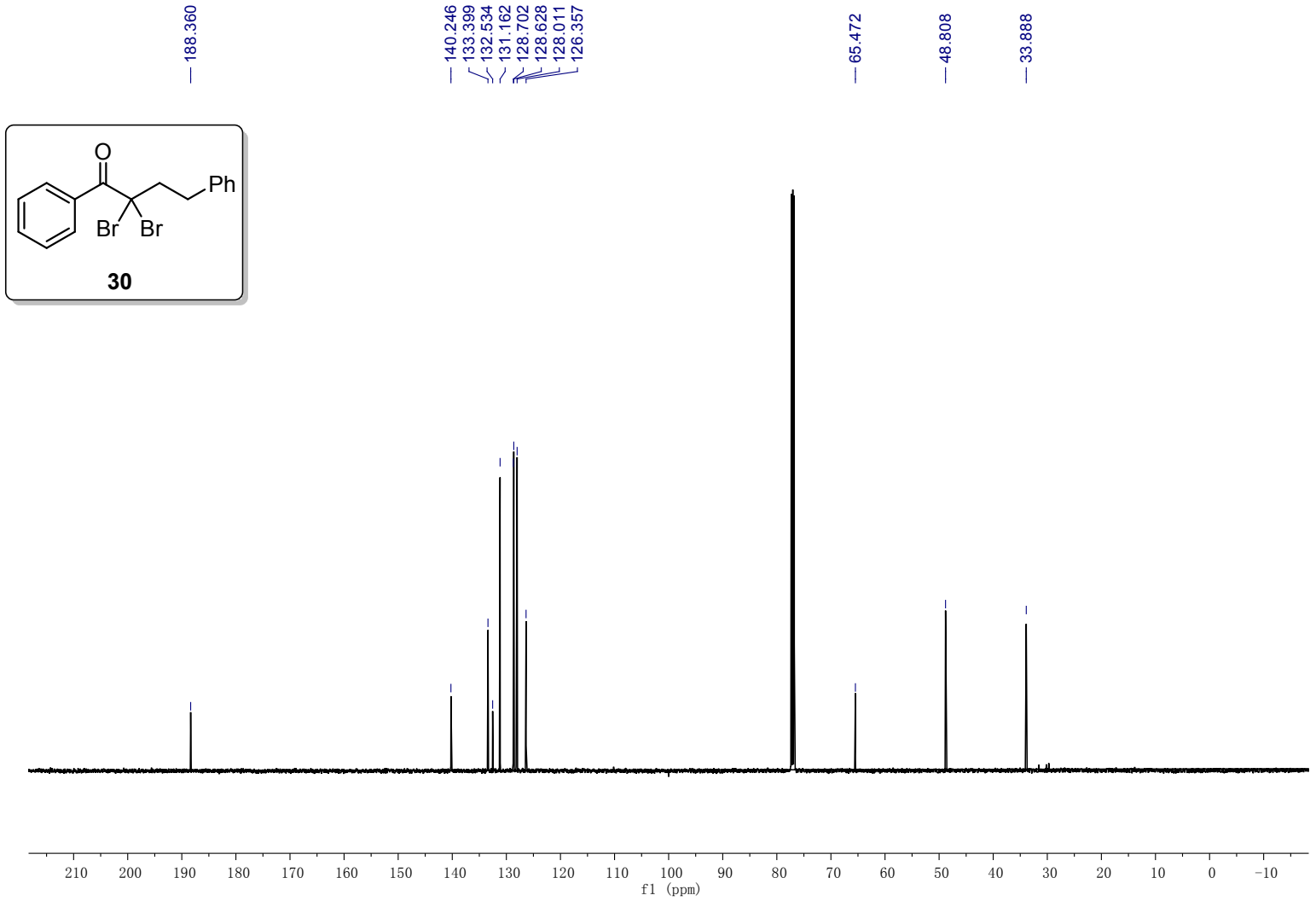
## $^{13}$C NMR of 29


186.970
133.783
132.000
130.932
128.119
60.912
53.684
O
Cl
Br
Br
29
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)

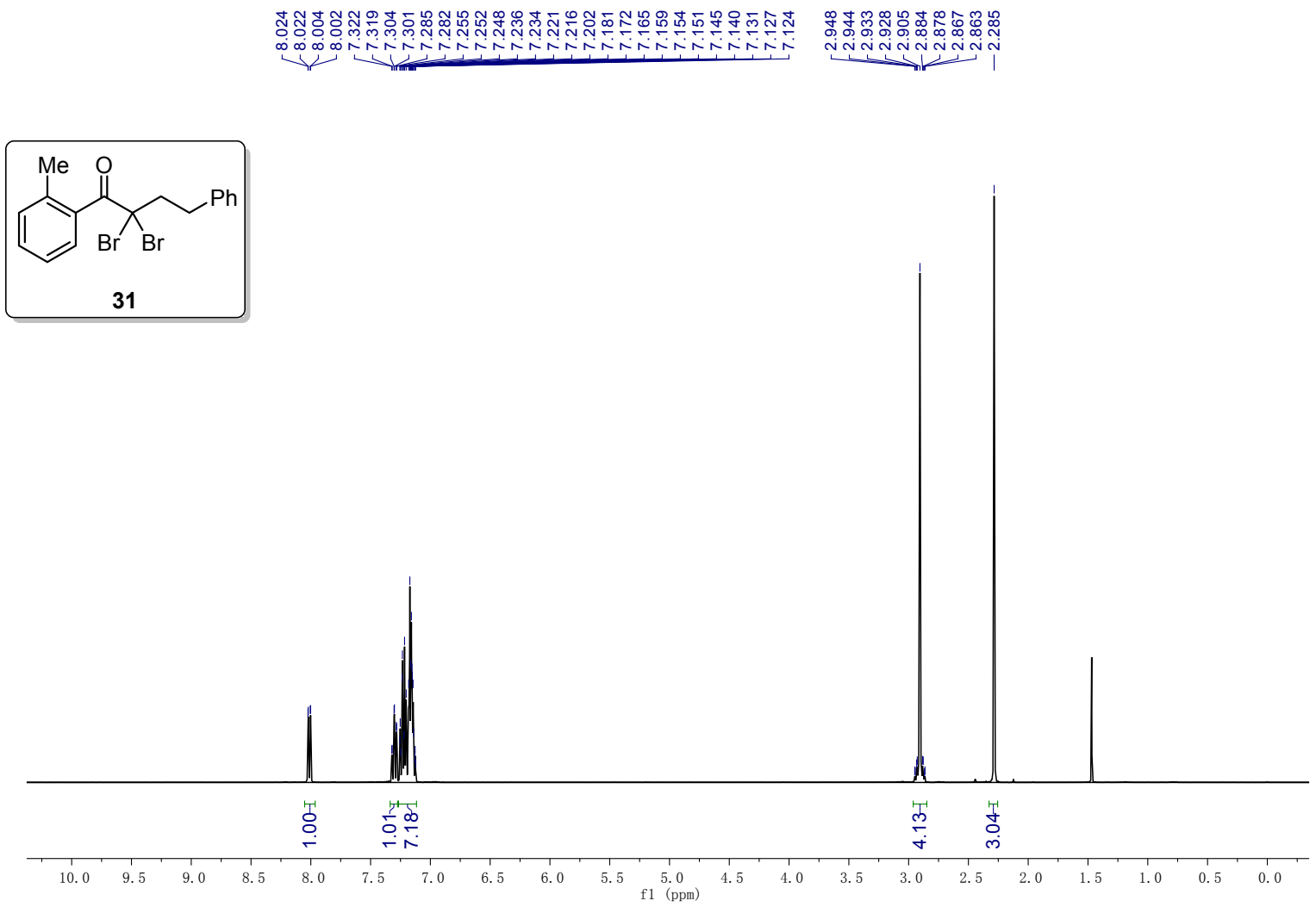
## $^{1}$H NMR of 30


8.419
8.399
7.636
7.618
7.600
7.528
7.508
7.489
7.371
7.352
7.334
7.312
7.295
7.283
7.260
7.242
3.108
3.101
3.092
3.082
3.064
3.041
3.031
3.022
3.012
3.003
2.996
O
Ph
Br
Br
30
1.98
1.00
2.05
1.97
3.12
2.03
2.05
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

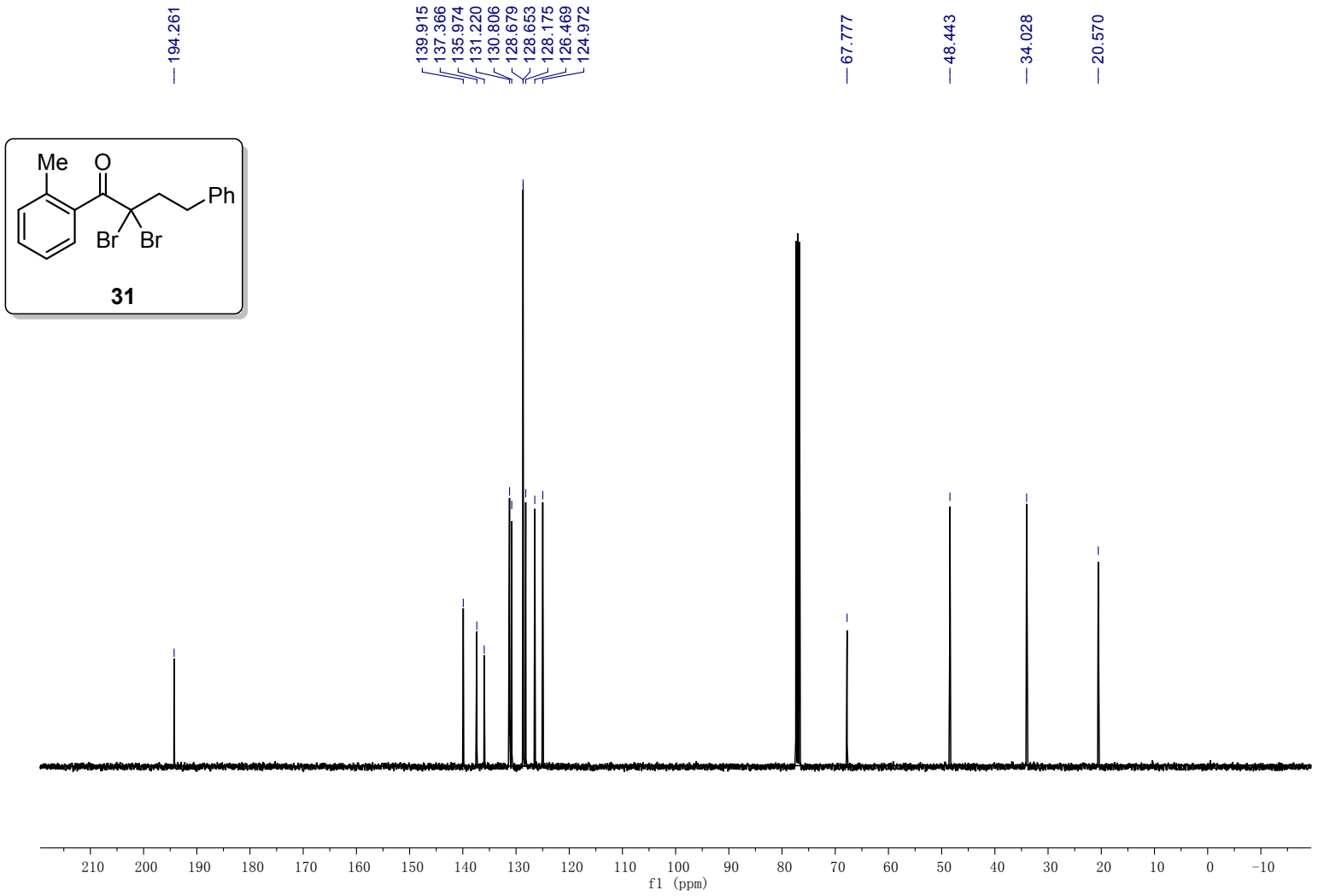
## $^{13}$C NMR of 30


188.360
140.246
133.399
132.534
131.162
128.702
128.628
128.011
126.357
65.472
48.808
33.888
O
Ph
Br
Br
30
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)

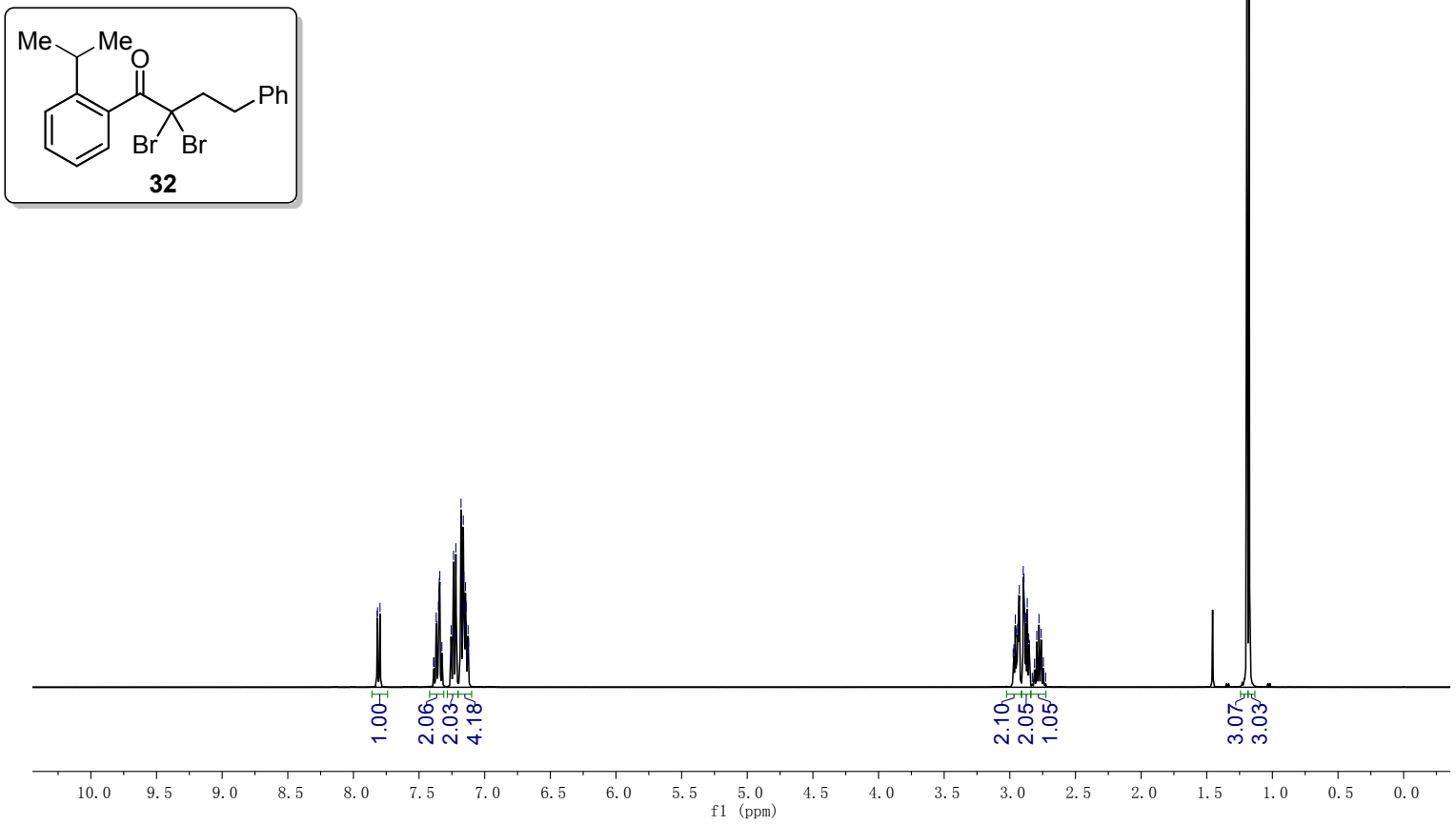
## $^1$H NMR of 31


8.024
8.022
8.004
8.002
7.322
7.319
7.304
7.301
7.285
7.282
7.255
7.252
7.248
7.236
7.234
7.221
7.216
7.202
7.181
7.172
7.165
7.159
7.154
7.151
7.145
7.140
7.131
7.127
7.124
2.948
2.944
2.933
2.928
2.905
2.884
2.878
2.867
2.863
2.285
Me
O
Ph
Br
Br
31
1.00
1.01
7.18
4.13
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

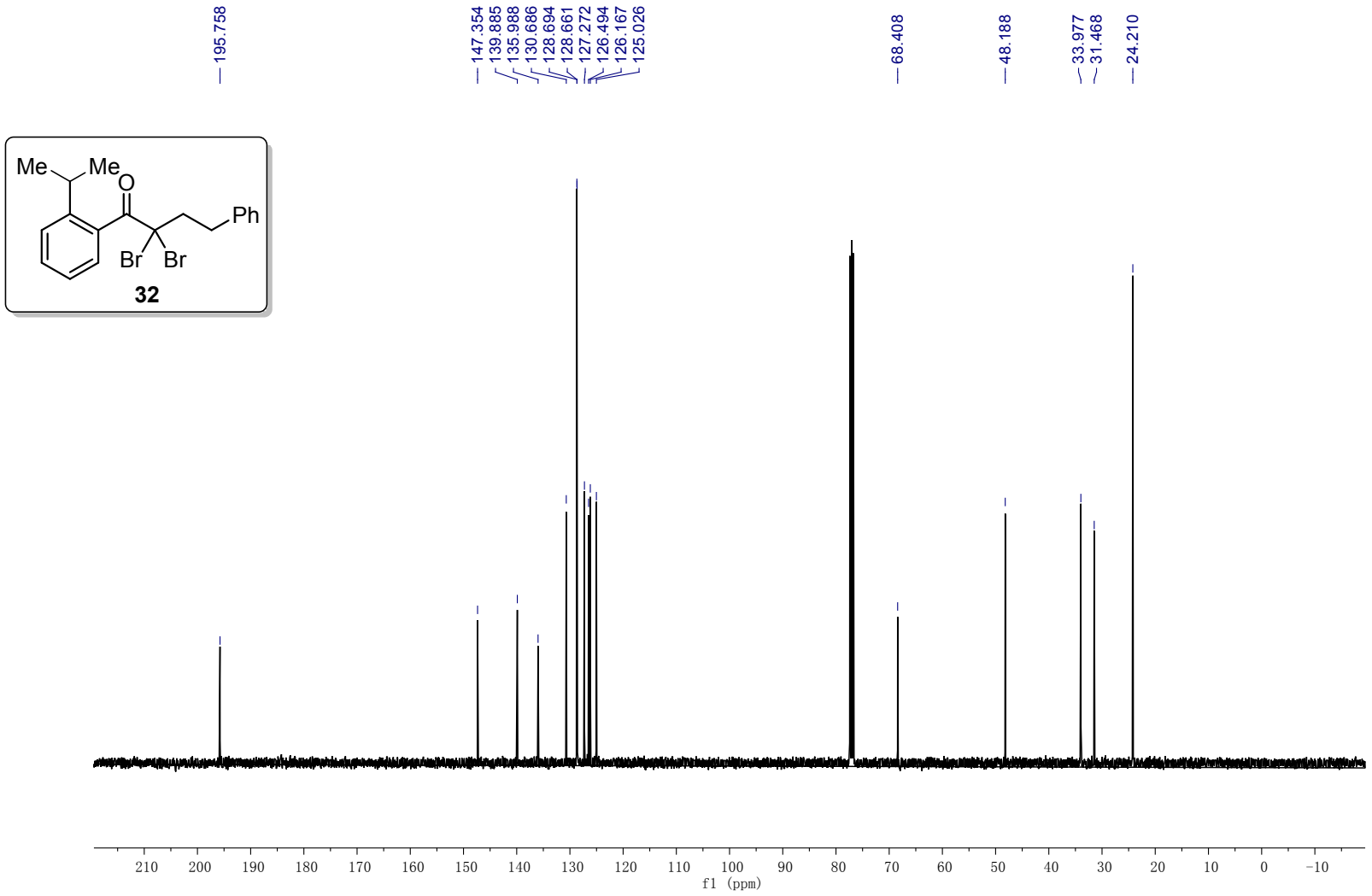
## $^{13}$C NMR of 31


194.261
139.915
137.366
135.974
131.220
130.806
128.679
128.653
128.175
126.469
124.972
67.777
48.443
34.028
20.570
Me
O
Ph
Br
Br
31
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)

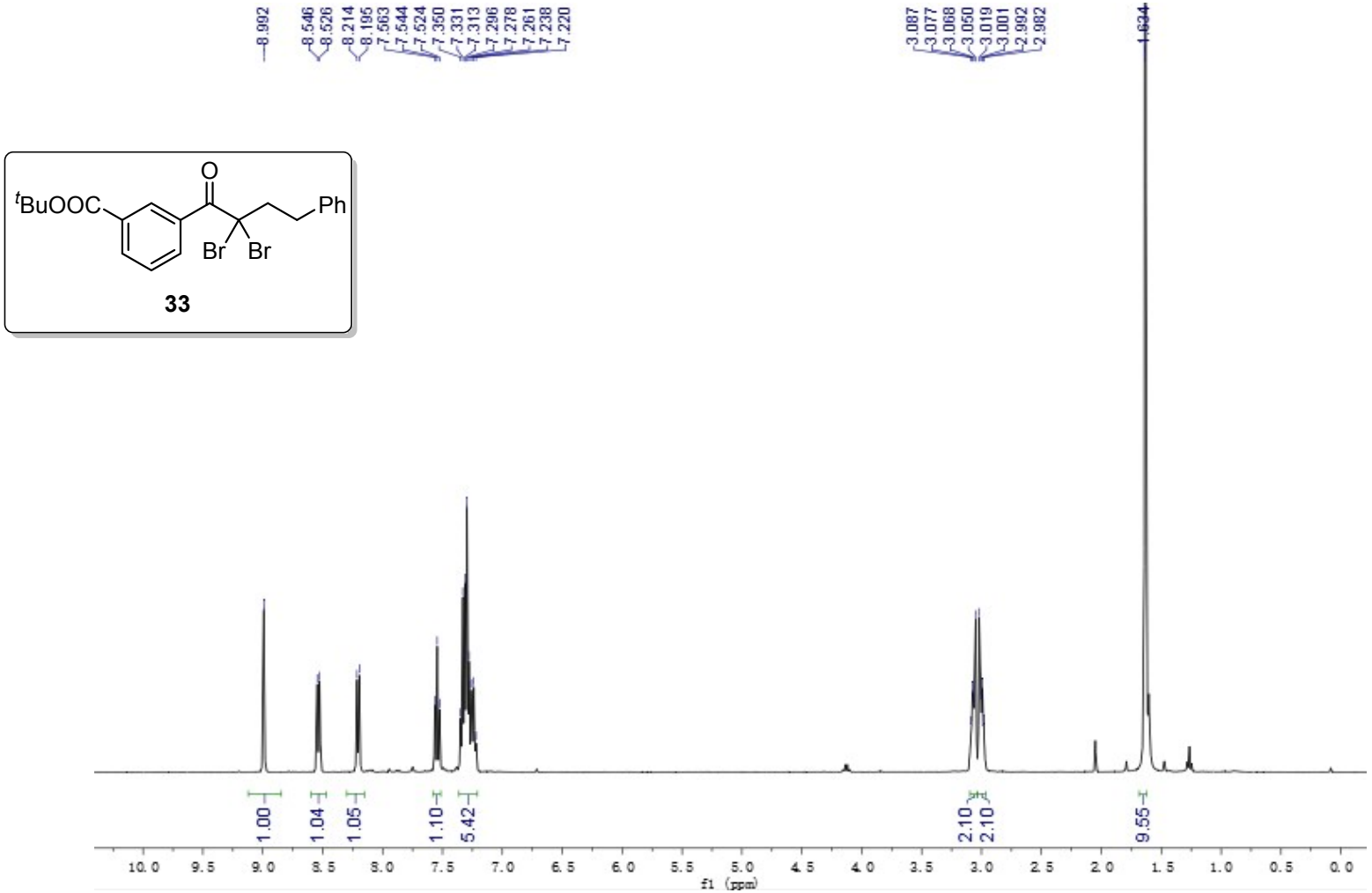
## $^1$H NMR of 32


7.819
7.817
7.798
7.370
7.367
7.353
7.349
7.346
7.342
7.256
7.238
7.224
7.220
7.180
7.163
7.159
7.156
7.147
7.143
7.142
7.139
2.969
2.958
2.949
2.941
2.933
2.928
2.898
2.892
2.887
2.884
2.876
2.867
2.856
2.851
2.829
2.812
2.795
2.778
2.761
2.744
2.727
1.194
1.177
Me
Me
O
Ph
Br
Br
32
1.00
2.06
2.03
4.18
2.10
2.05
1.05
3.07
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

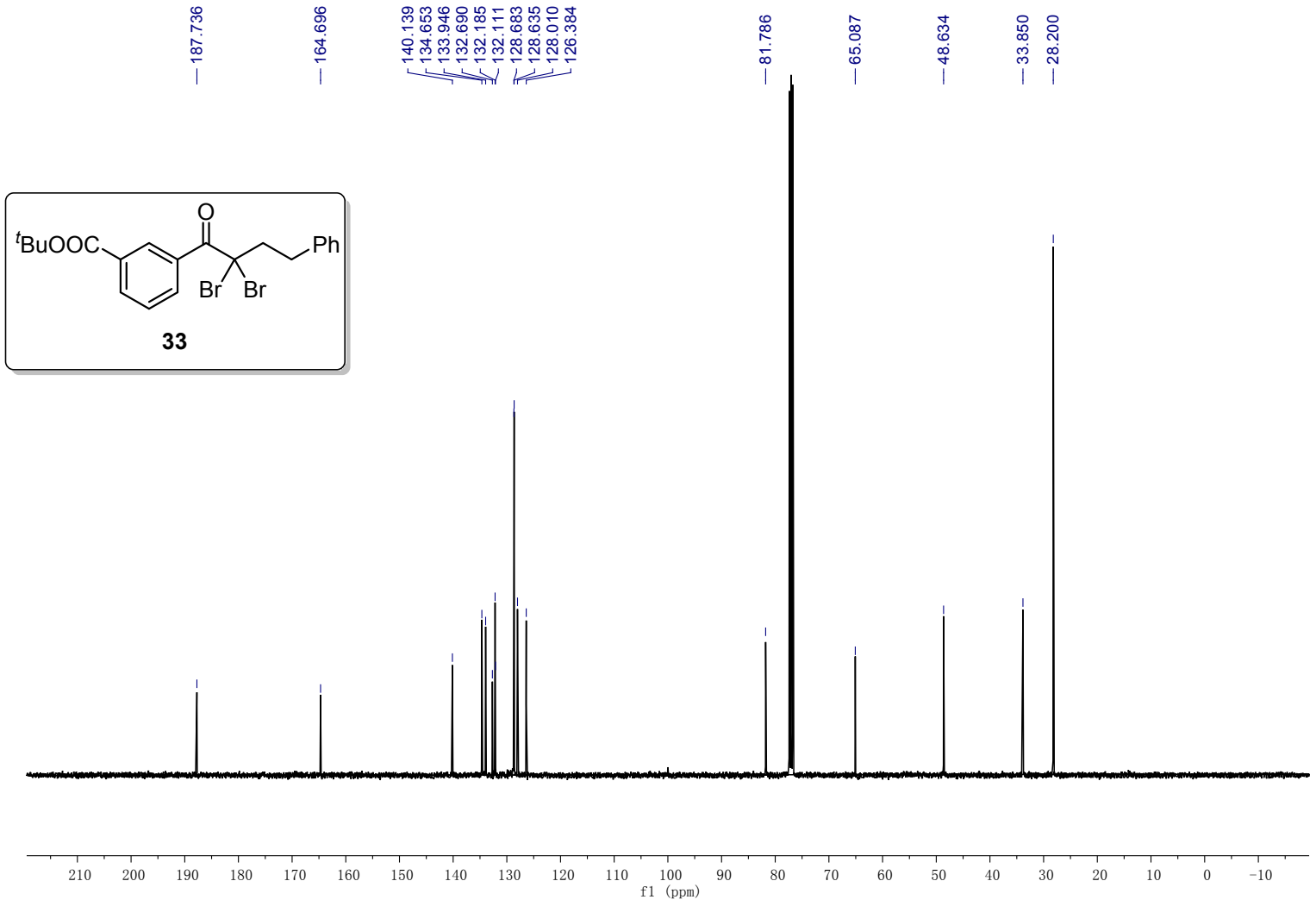
## $^{13}$C NMR of 32


195.758
147.354
139.885
135.988
130.686
128.694
128.661
127.272
126.494
126.167
125.026
68.408
48.188
33.977
31.468
24.210
Me
Me
O
Ph
Br
Br
32
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)

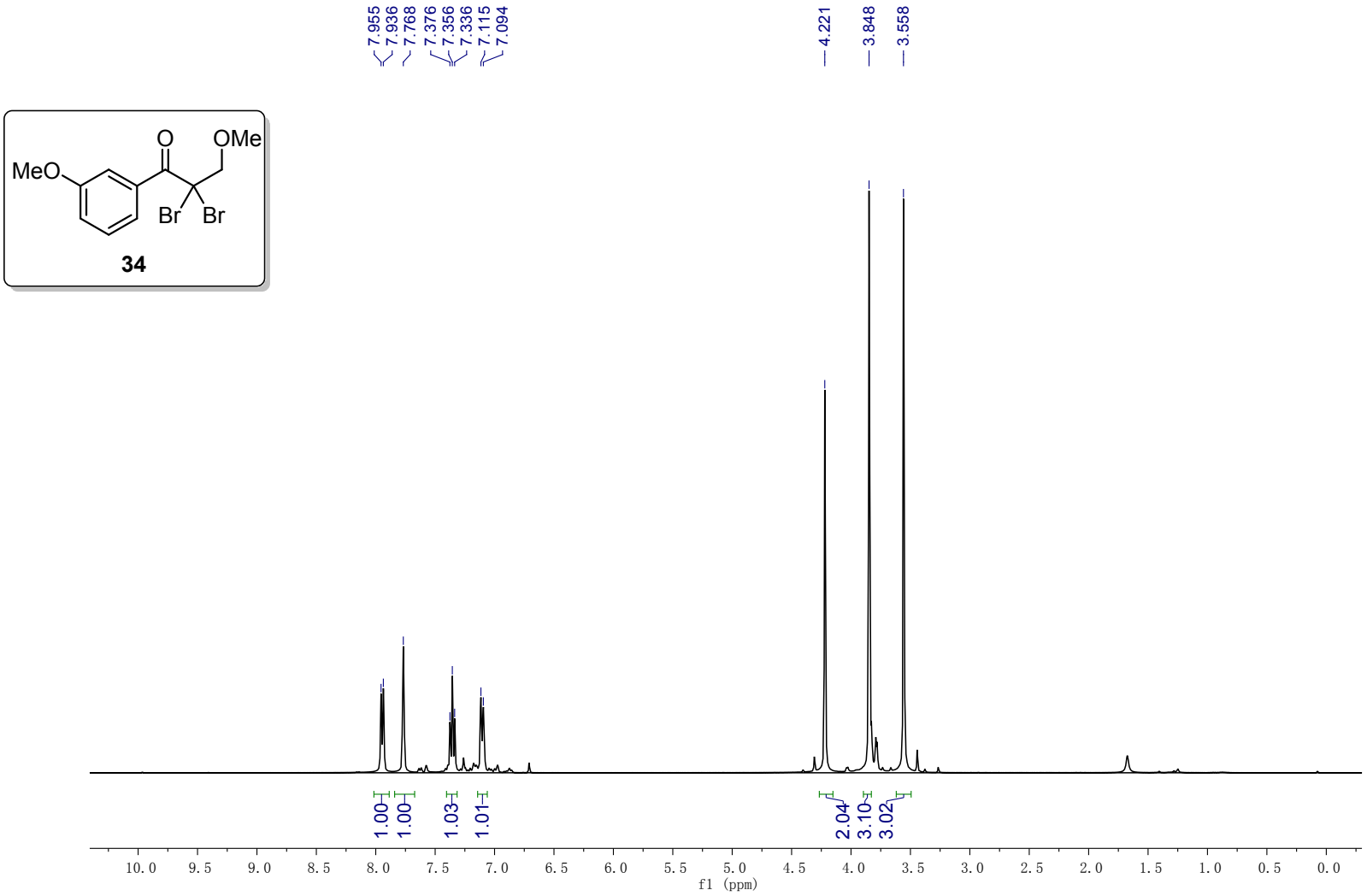
**$^1$H NMR of 33**


8.992
8.546
8.526
8.214
8.195
7.563
7.544
7.524
7.350
7.331
7.313
7.296
7.278
7.261
7.238
7.220
3.087
3.077
3.068
3.050
3.019
3.001
2.992
2.982
1.634
tBuOOC
O
Ph
Br
Br
33
1.00
1.04
1.05
1.10
5.42
2.10
2.10
9.55
f1 (ppm)

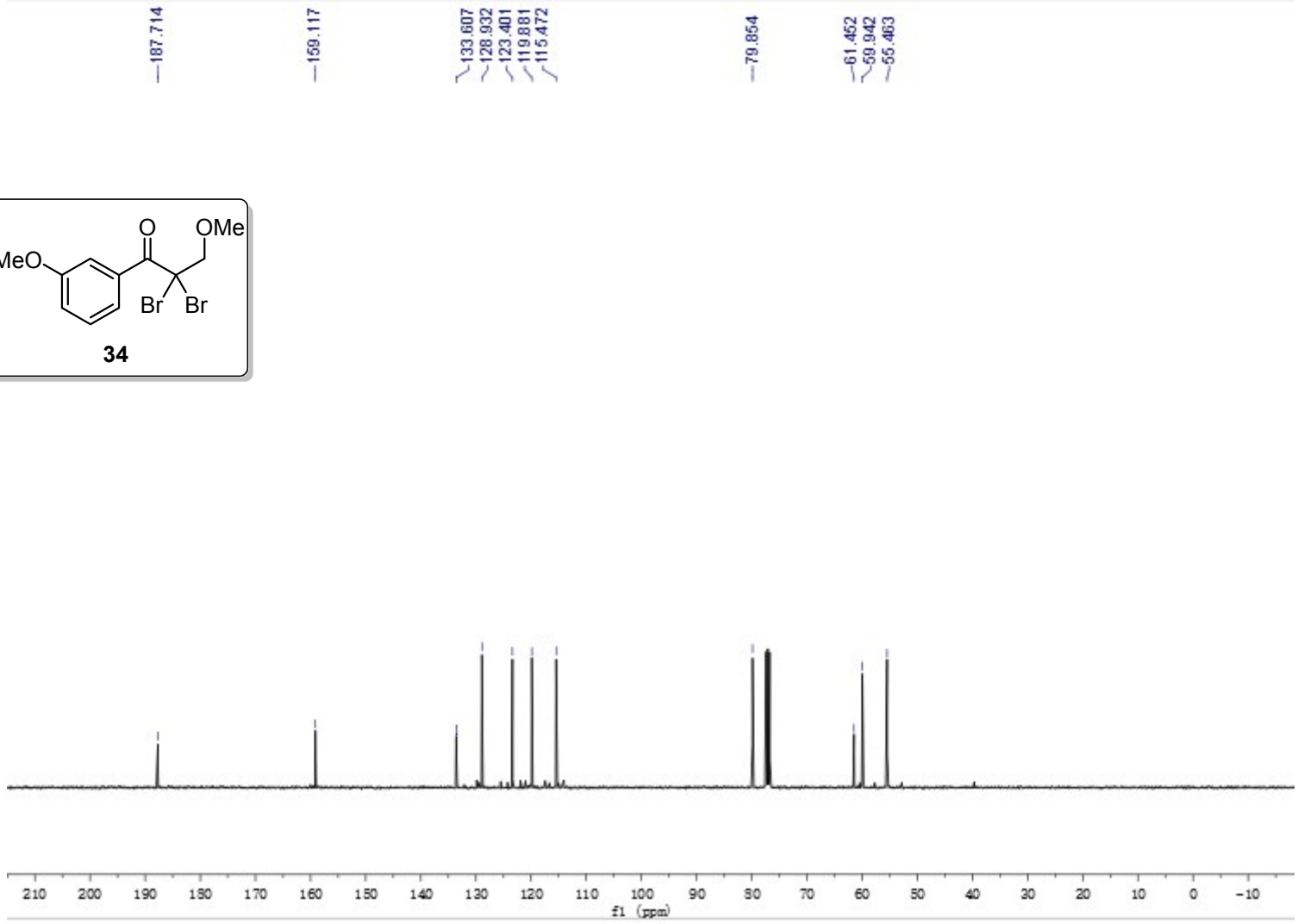
## $^{13}$C NMR of 33


187.736
164.696
140.139
134.653
133.946
132.690
132.185
132.111
128.683
128.635
128.010
126.384
81.786
65.087
48.634
33.850
28.200
tBuOOC
O
Ph
Br
Br
33
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)

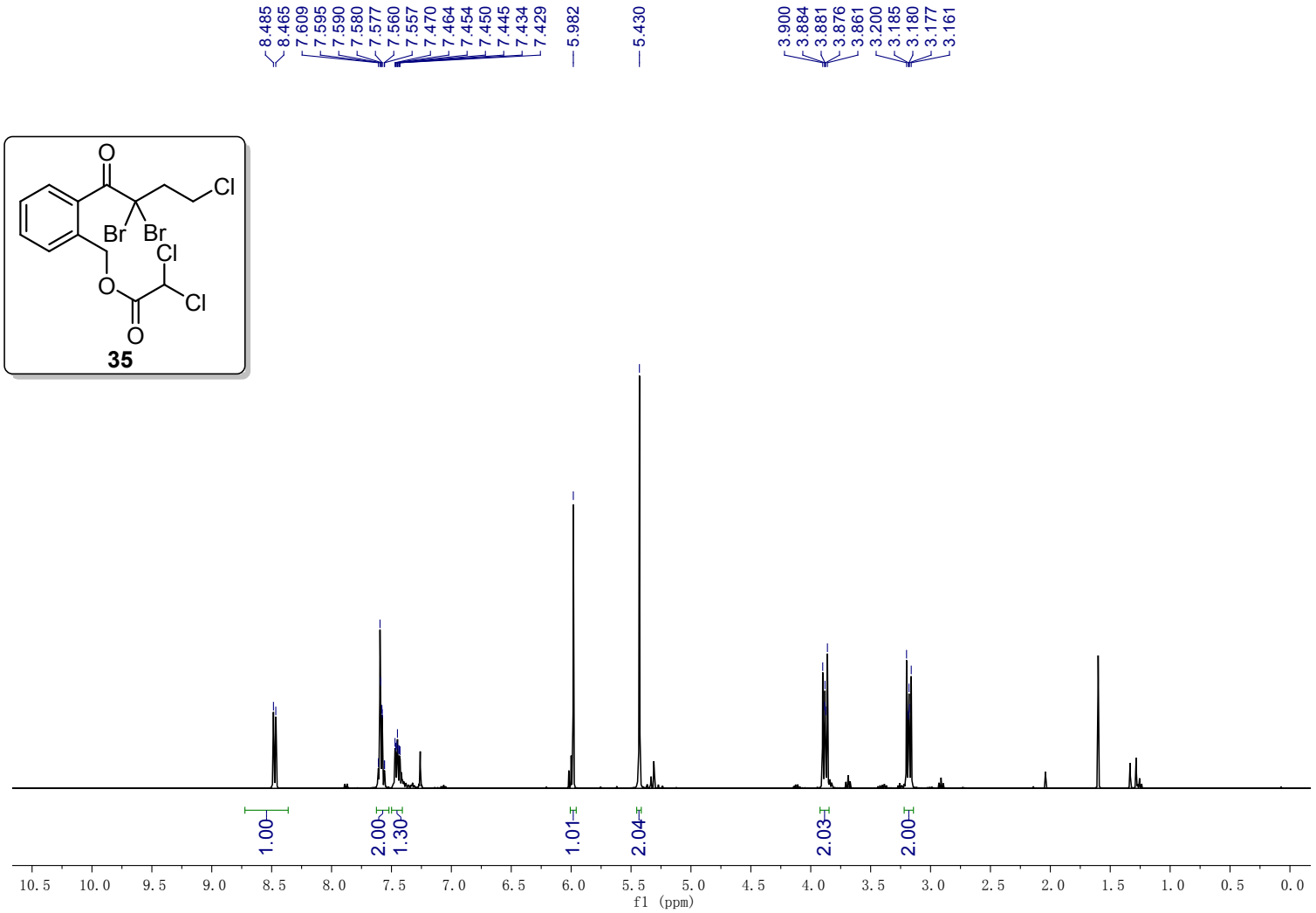
## $^{1}$H NMR of 34


7.955
7.936
7.768
7.376
7.356
7.336
7.115
7.094
4.221
3.848
3.558
MeO
O
OMe
Br
Br
34
1.00
1.00
1.03
1.01
2.04
3.10
3.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

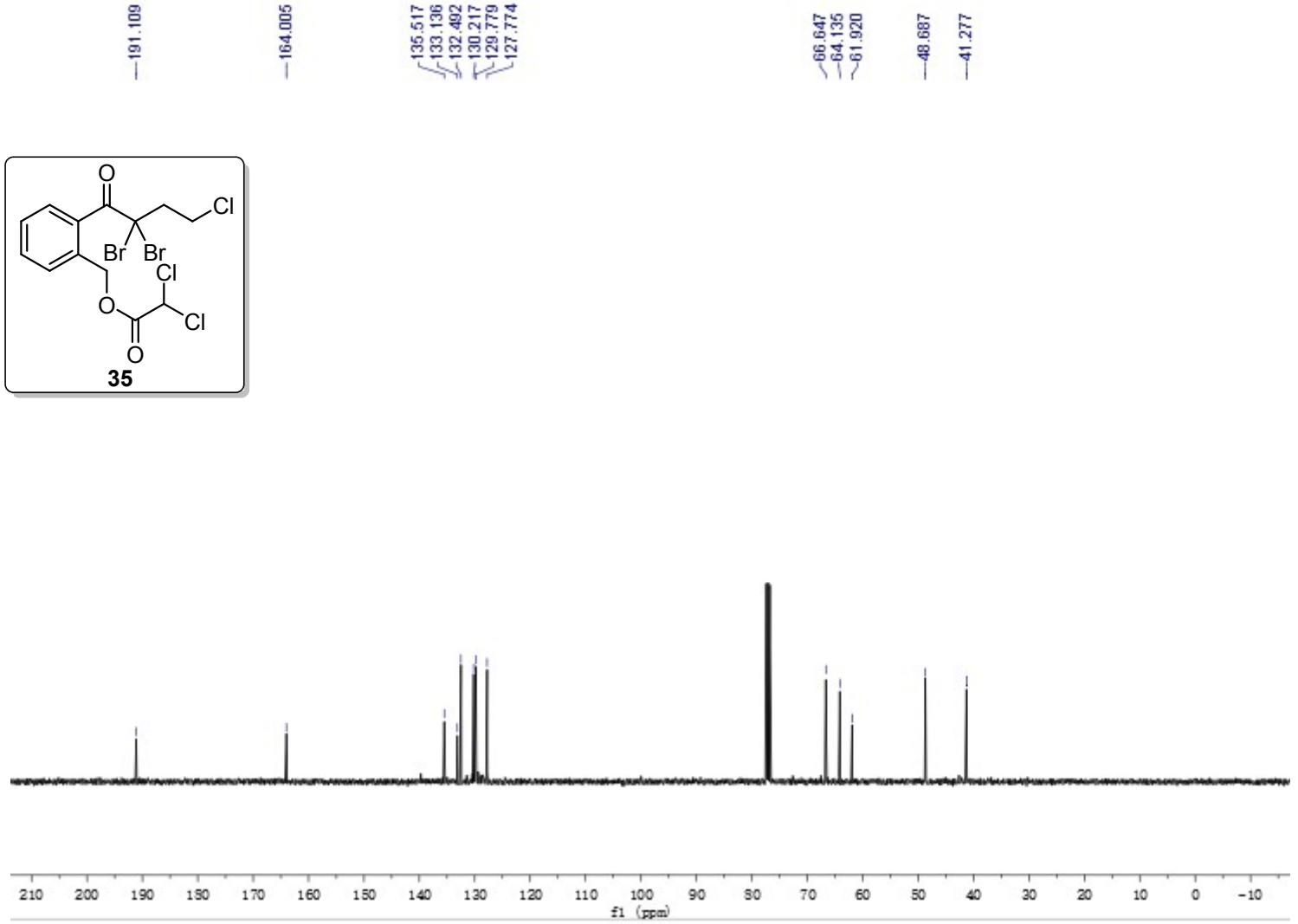
## $^{13}$C NMR of 34


187.714
159.117
133.607
128.932
123.401
119.881
115.472
79.854
61.452
59.942
55.463
O
OMe
MeO
Br
Br
34
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)

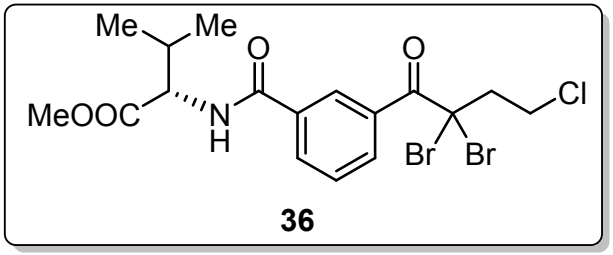
## $^{1}$H NMR of 35


8.485
8.465
7.609
7.595
7.590
7.580
7.577
7.560
7.557
7.470
7.464
7.454
7.450
7.445
7.434
7.429
5.982
5.430
3.900
3.884
3.881
3.876
3.861
3.200
3.185
3.180
3.177
3.161
O
Cl
Br
Br
Cl
O
Cl
O
35
1.00
2.00
1.30
1.01
2.04
2.03
2.00
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
f1 (ppm)

## $^{13}$C NMR of 35

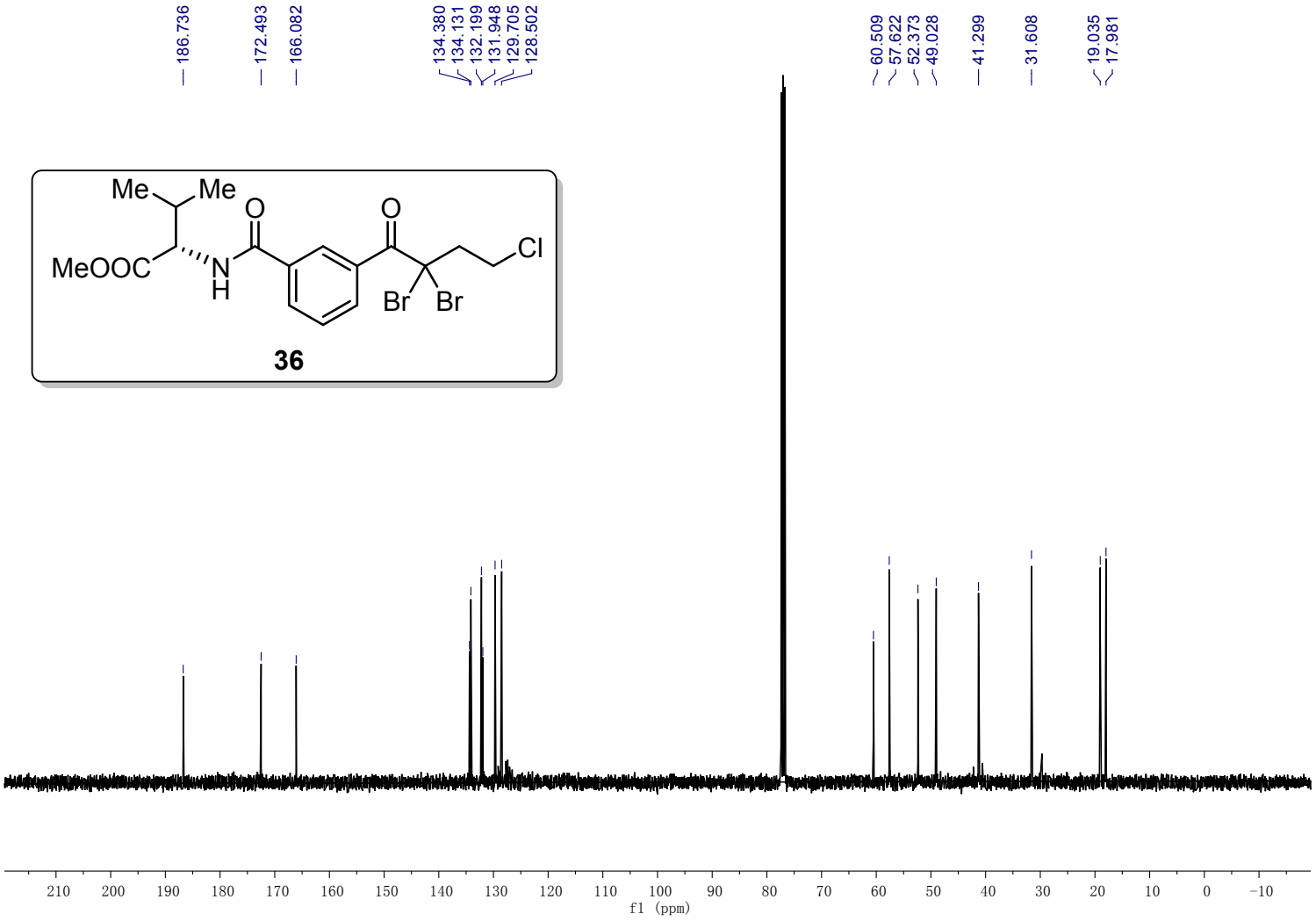

191.109
164.005
135.517
133.136
132.492
130.217
129.779
127.774
66.647
64.135
61.920
48.687
41.277
O
Cl
Br
Br
Cl
O
Cl
O
35
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

**$^1$H NMR of 36**

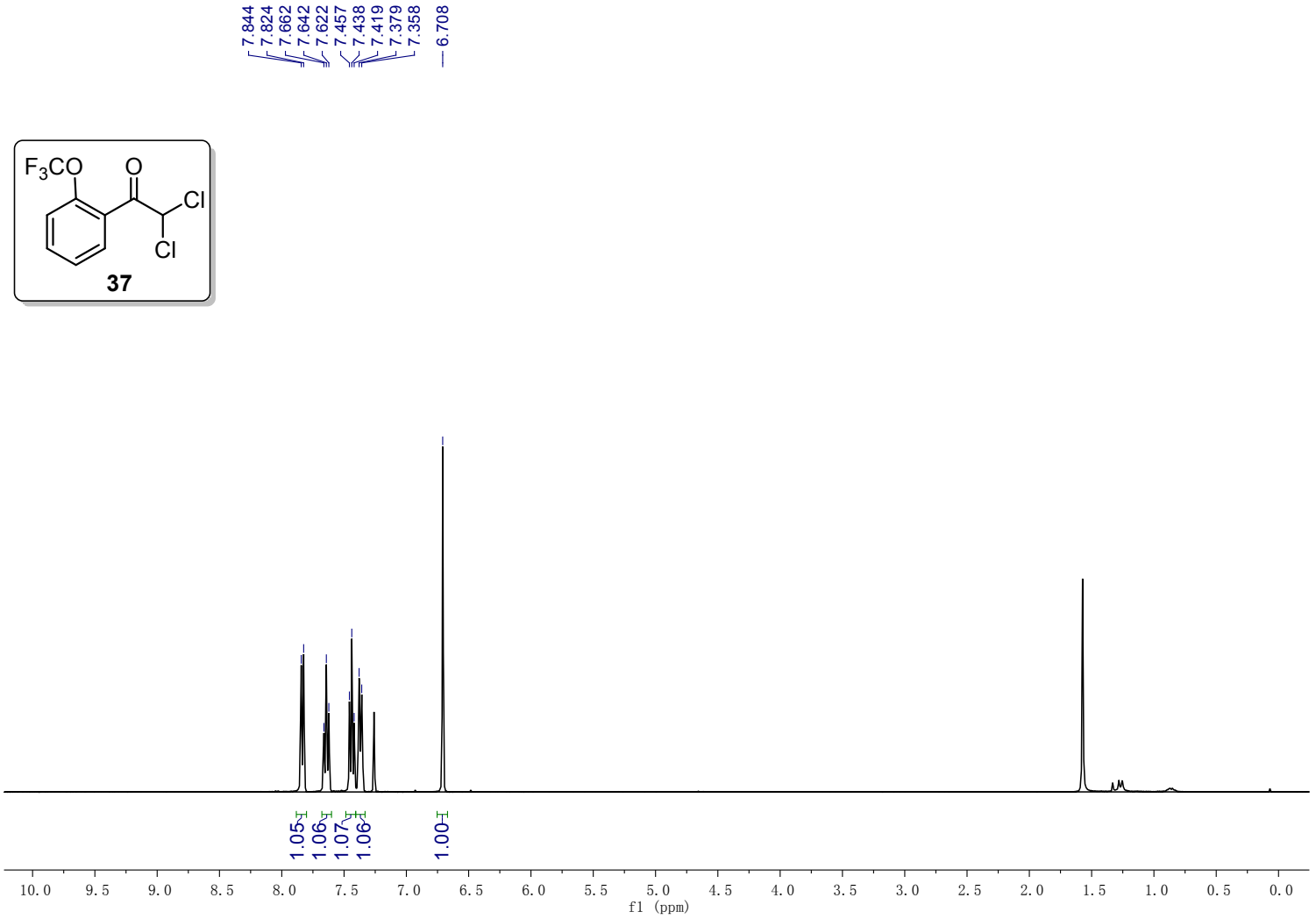



**36**

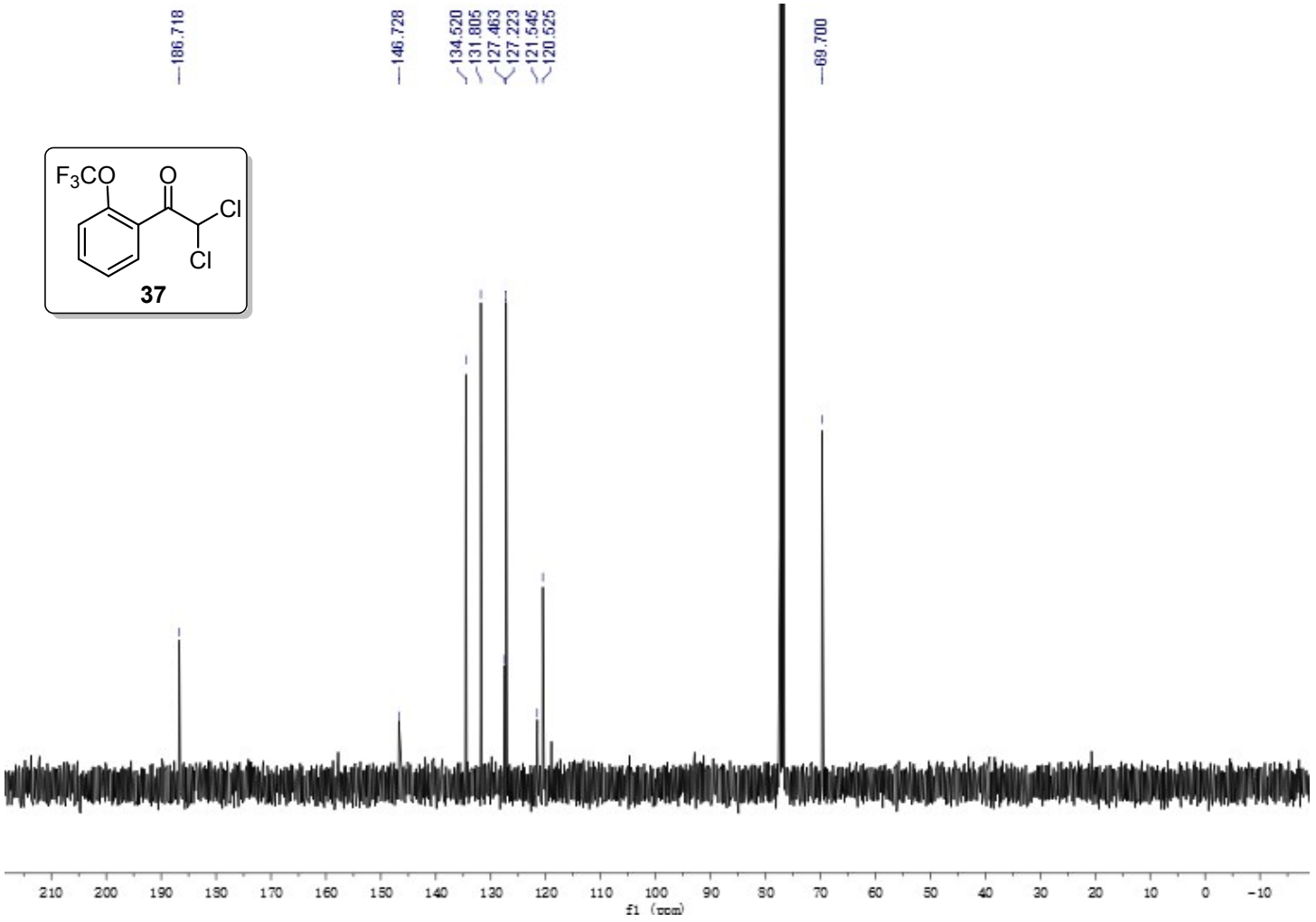
## $^{13}$C NMR of 36


186.736
172.493
166.082
134.380
134.131
132.199
131.948
129.705
128.502
60.509
57.622
52.373
49.028
41.299
31.608
19.035
17.981
Me
Me
O
O
MeOOC
N
H
Cl
Br
Br
36
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)

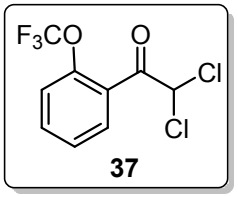
**$^1$H NMR of** **37**


7.844
7.824
7.662
7.642
7.622
7.457
7.438
7.419
7.379
7.358
6.708
F3CO
O
Cl
Cl
37
1.05
1.06
1.07
1.06
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

## $^{13}$C NMR of 37

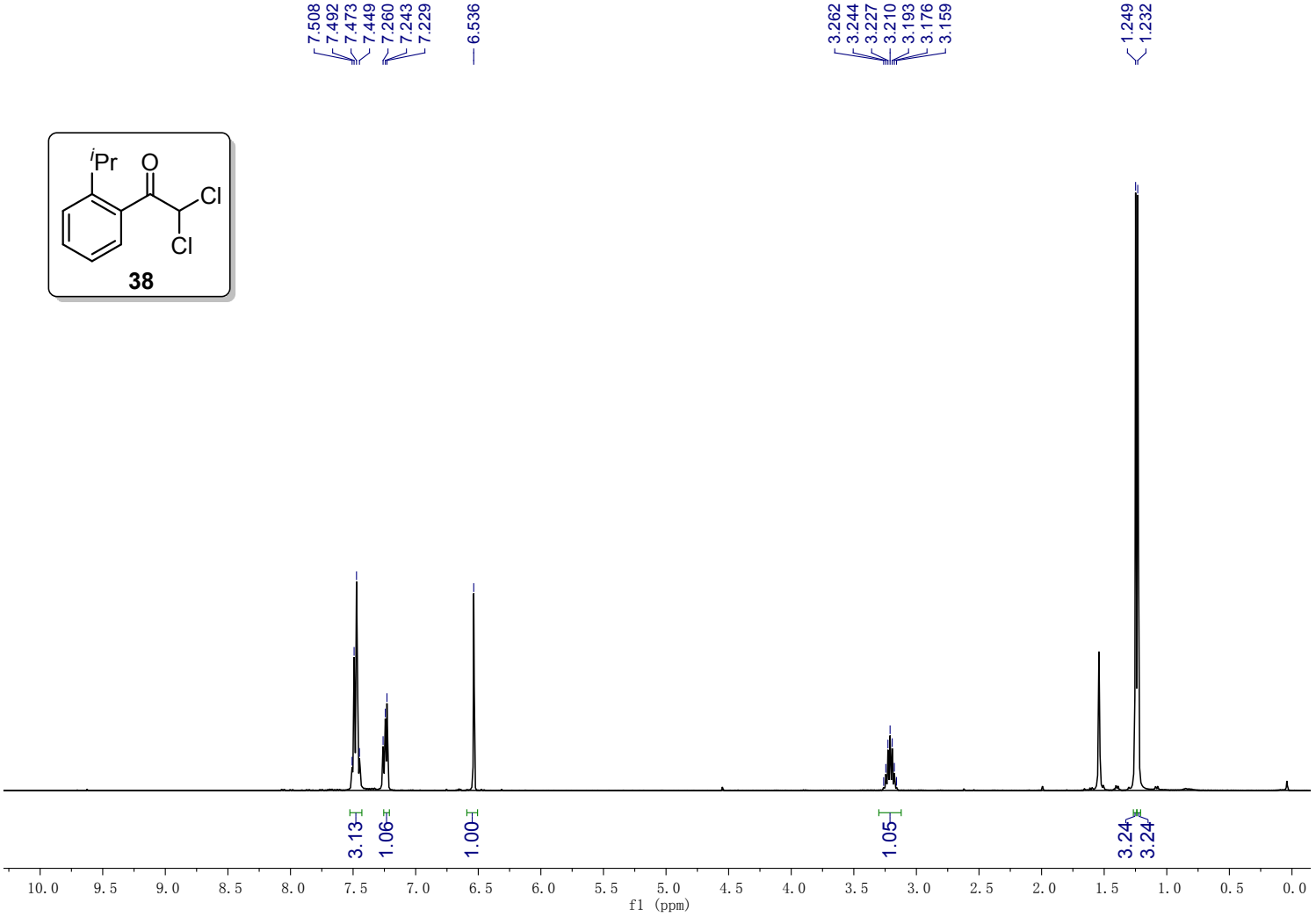

186.718
146.728
134.520
131.805
127.463
127.223
121.545
120.525
69.700
F3CO
O
Cl
Cl
37
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

## $^{19}$F NMR of 37

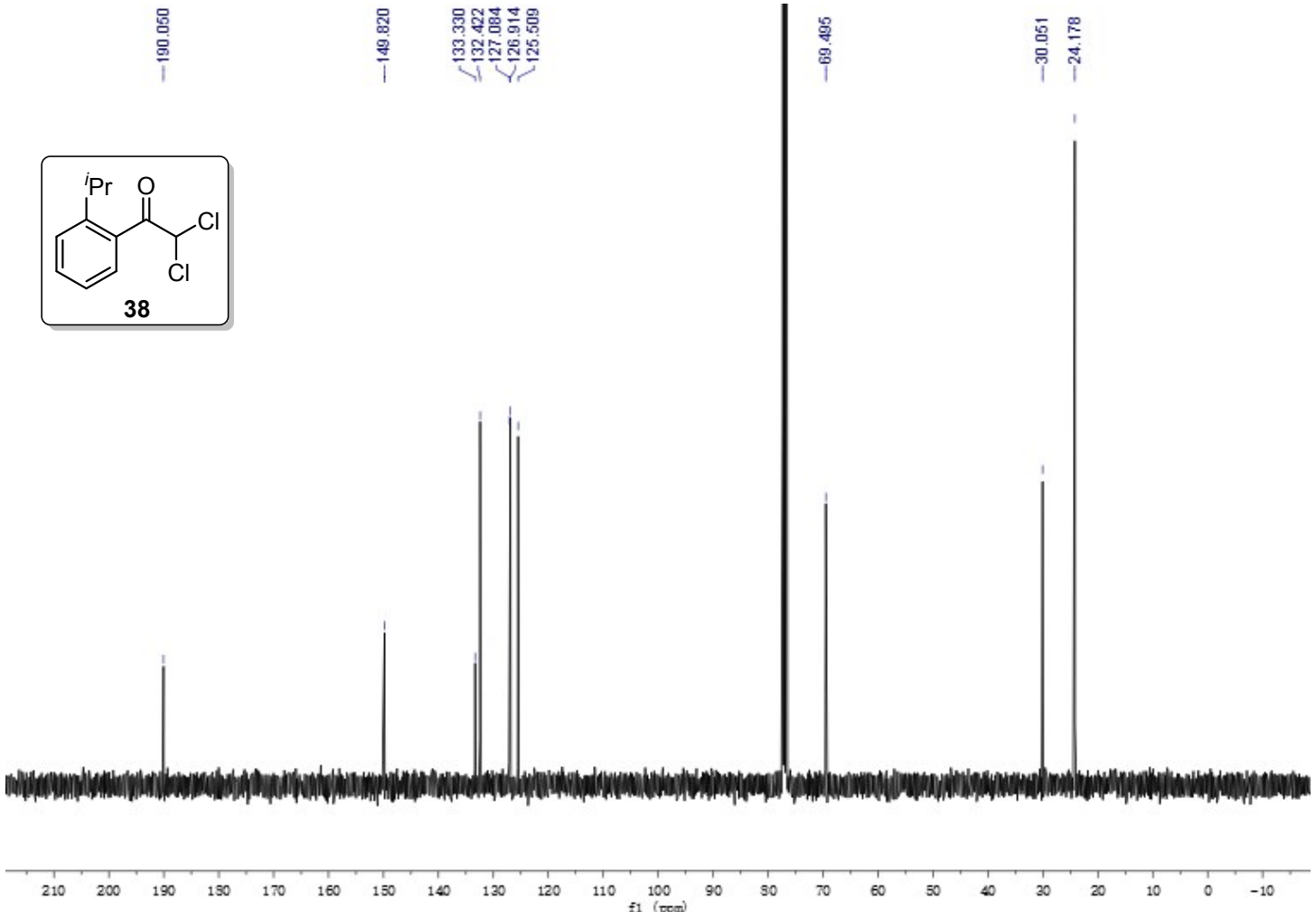



**37**

## $^{1}$H NMR of 38

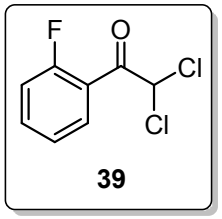

7.508
7.492
7.473
7.449
7.260
7.243
7.229
6.536
3.262
3.244
3.227
3.210
3.193
3.176
3.159
1.249
1.232
iPr
O
Cl
Cl
38
3.13
1.06
1.00
1.05
3.24
3.24
f1 (ppm)

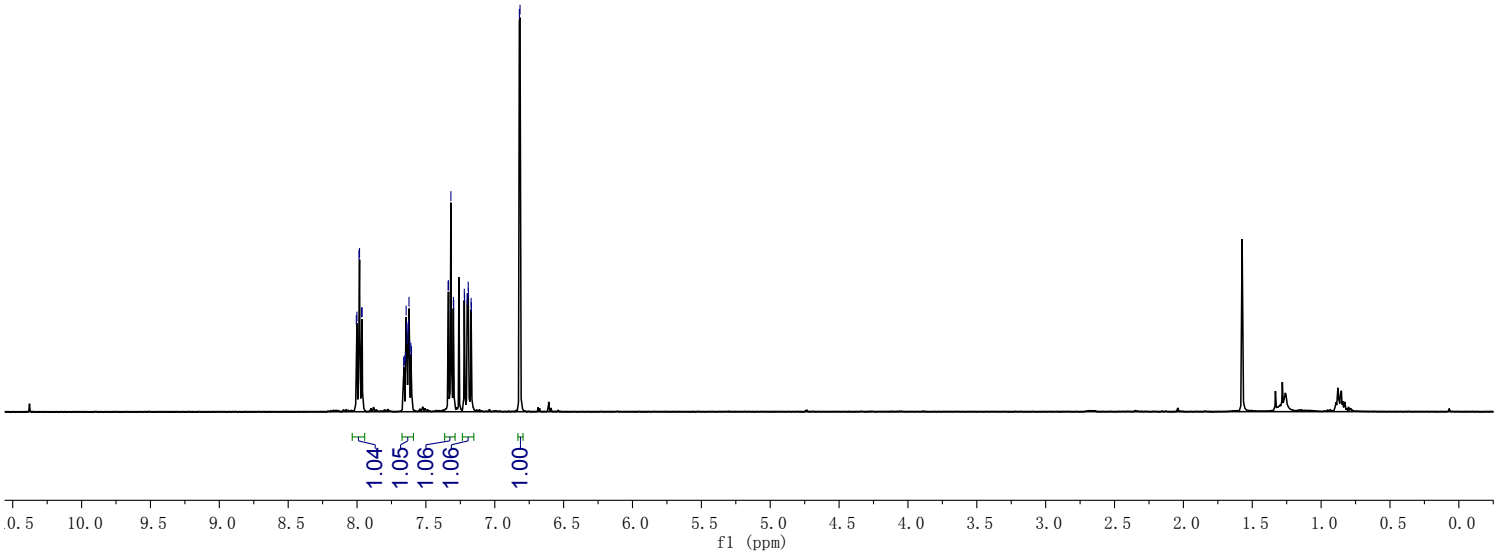
**$^{13}$C NMR of 38**


190.050
149.820
133.330
132.422
127.084
126.914
125.509
69.495
30.051
24.178
iPr
O
Cl
Cl
38
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)

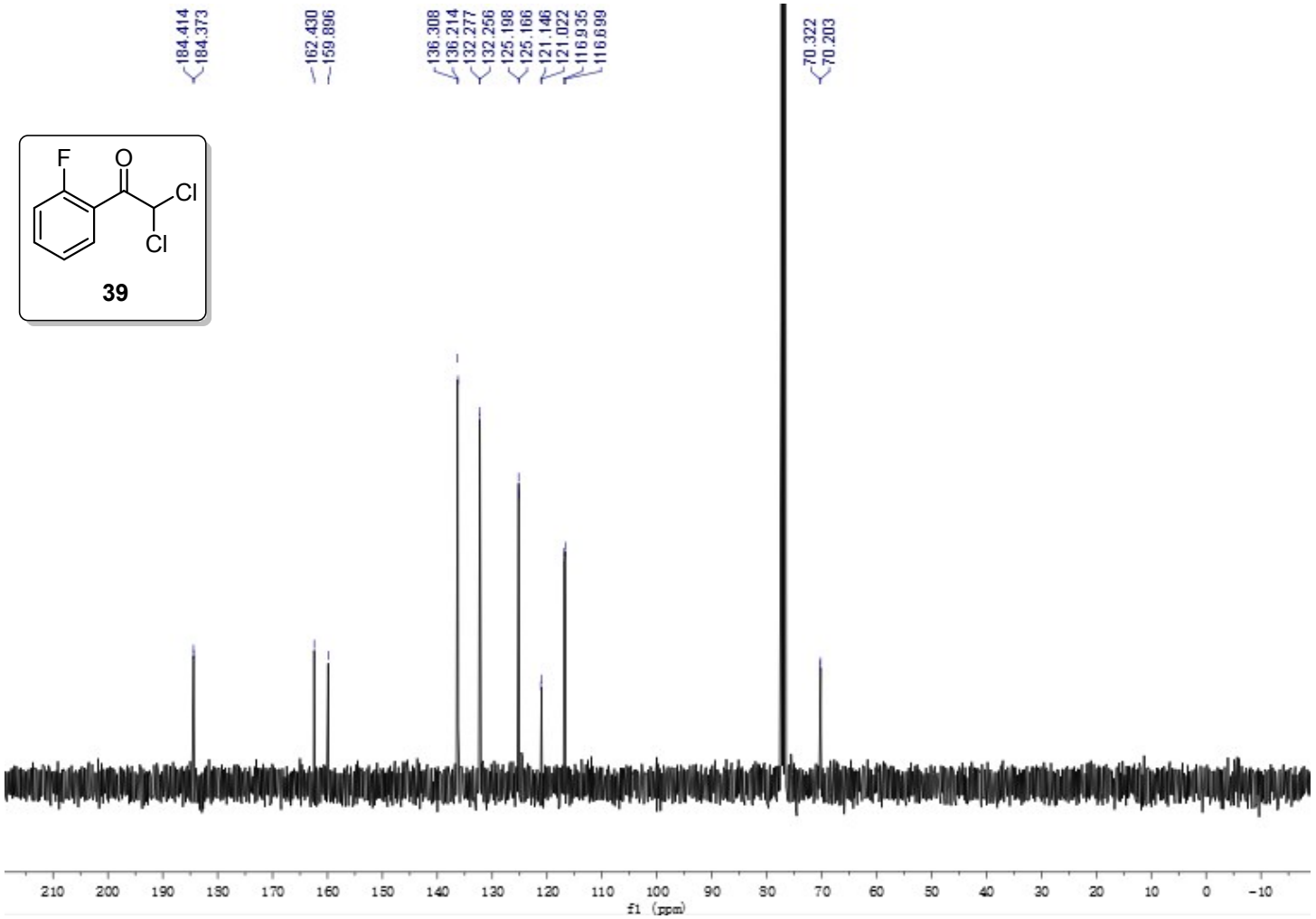
## $^{1}$H NMR of 39


8.005
8.001
7.986
7.982
7.967
7.963
7.643
7.640
7.625
7.623
7.339
7.336
7.319
7.301
7.298
7.221
7.219
7.200
7.198
7.193
7.191
7.172
6.822
6.816

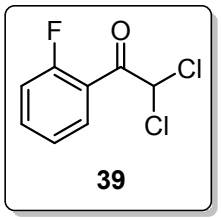

F
O
Cl
Cl
39


1.04
1.05
1.06
1.06
1.00
0.5
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
f1 (ppm)

**$^{13}$C NMR of 39**

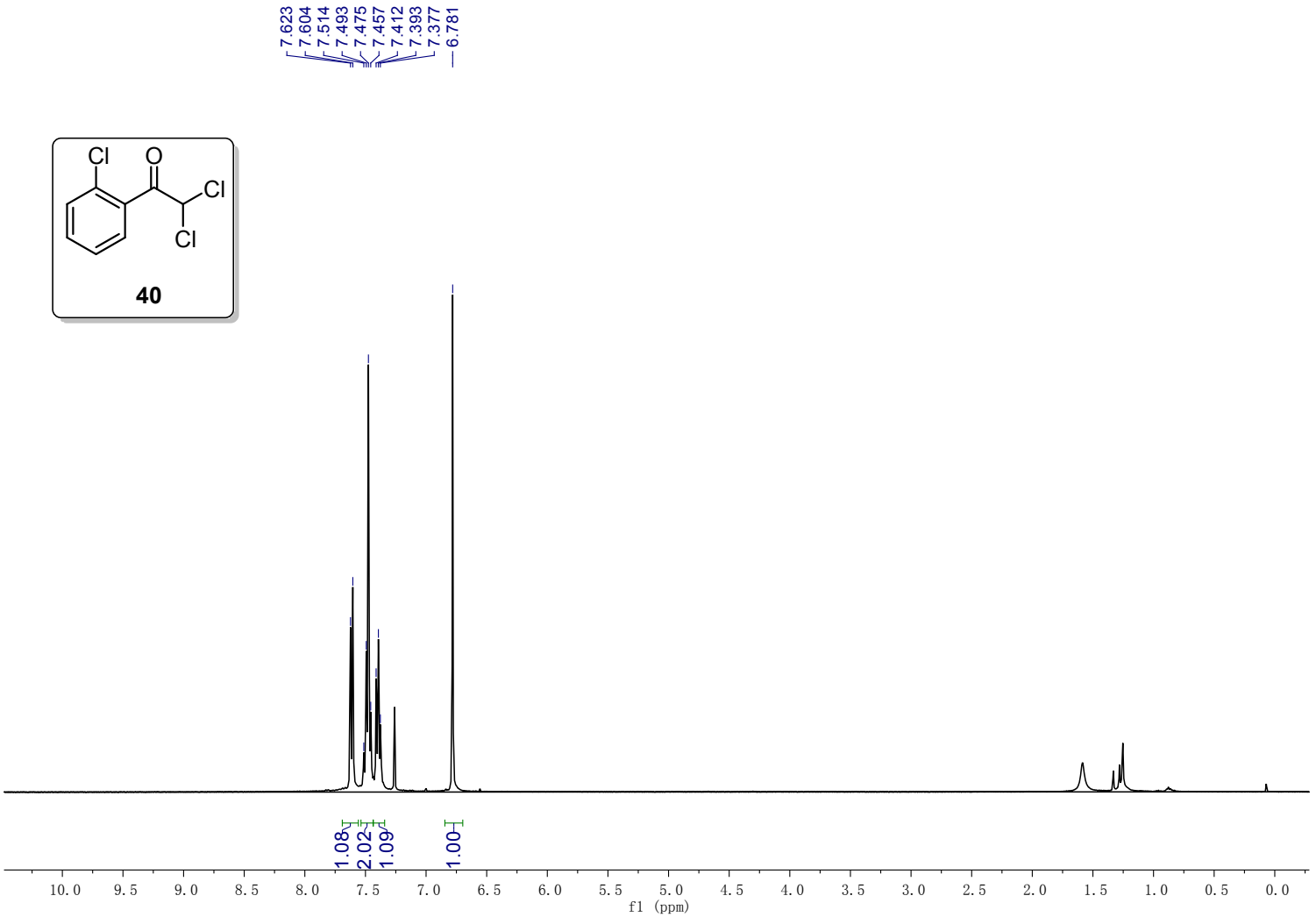

184.414
184.373
162.430
159.896
136.308
136.214
132.277
132.256
125.198
125.166
121.146
121.022
116.935
116.699
70.322
70.203
F
O
Cl
Cl
39
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

## $^{19}$F NMR of 39

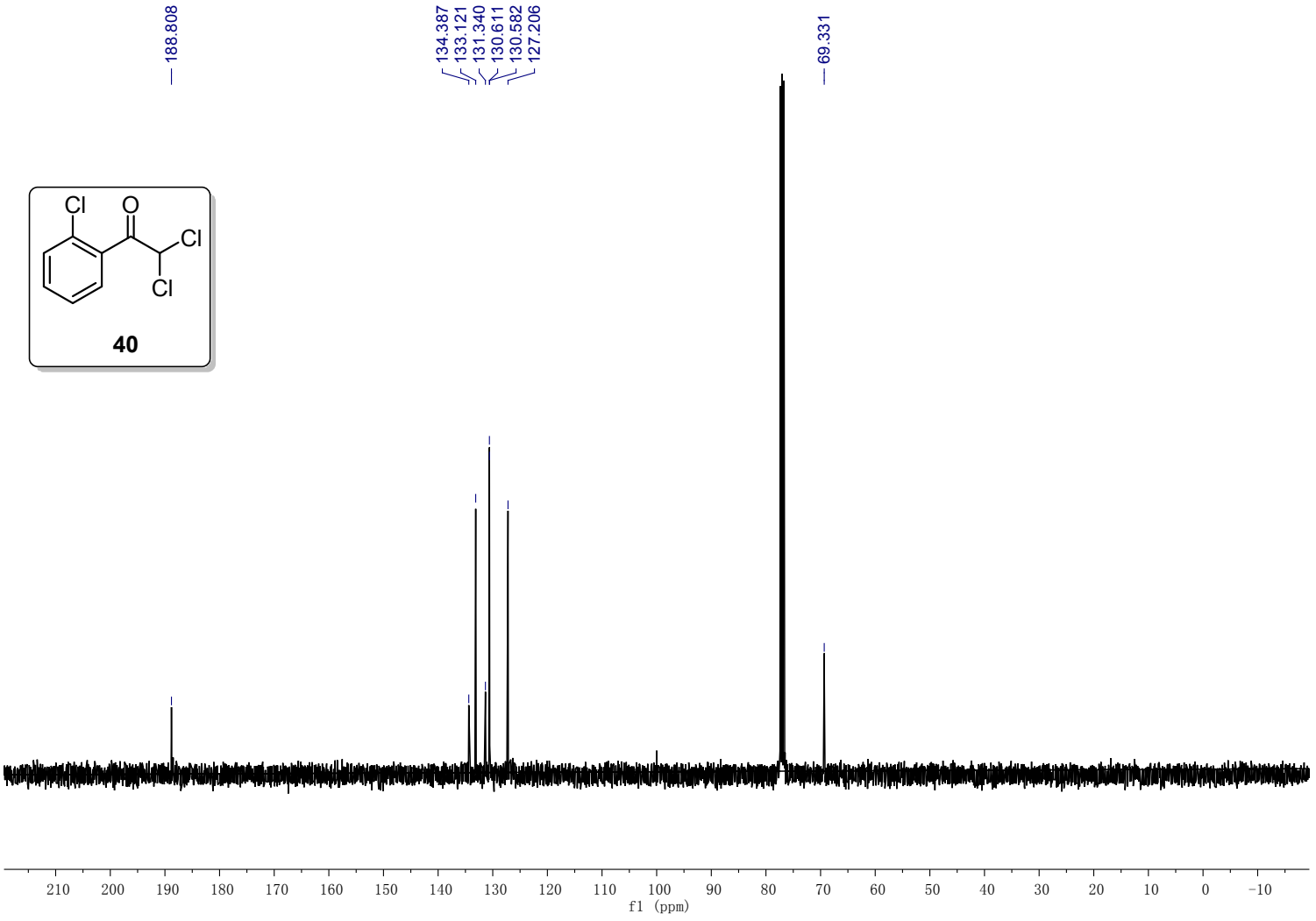



**39**

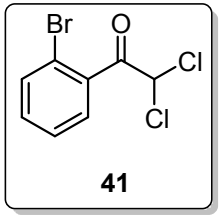
## $^{1}$H NMR of 40


7.623
7.604
7.514
7.493
7.475
7.457
7.412
7.393
7.377
6.781
Cl
O
Cl
Cl
40
1.08
2.02
1.09
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

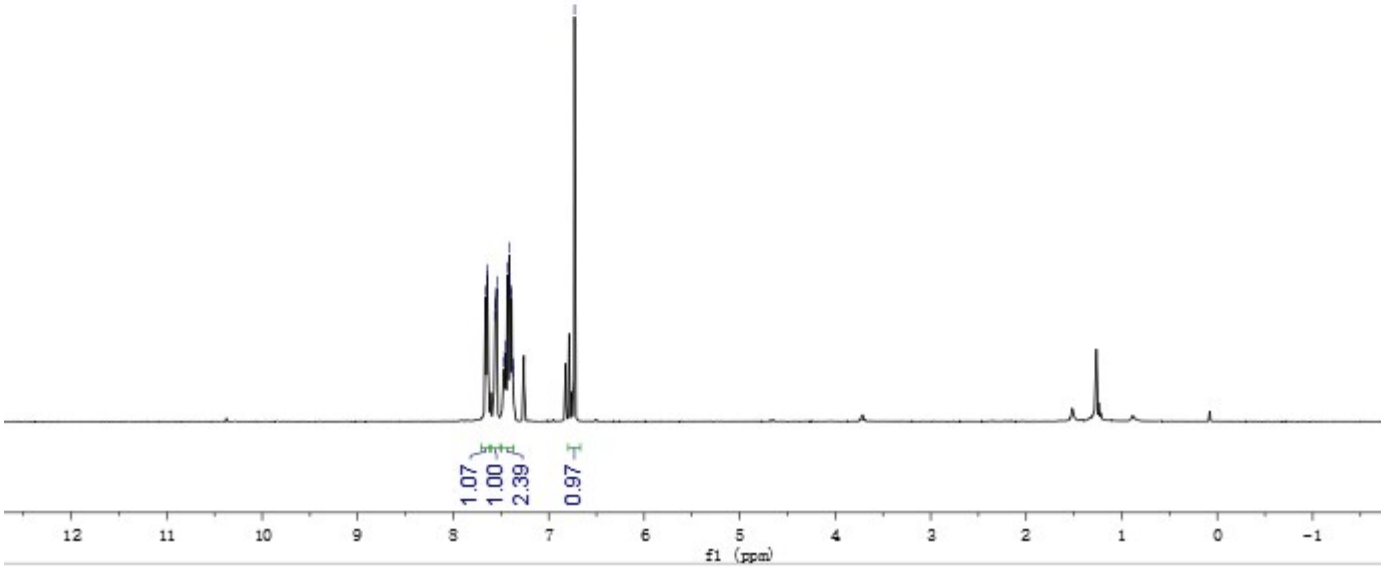
## $^{13}$C NMR of 40


188.808
134.387
133.121
131.340
130.611
130.582
127.206
69.331
Cl
O
Cl
Cl
40
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)

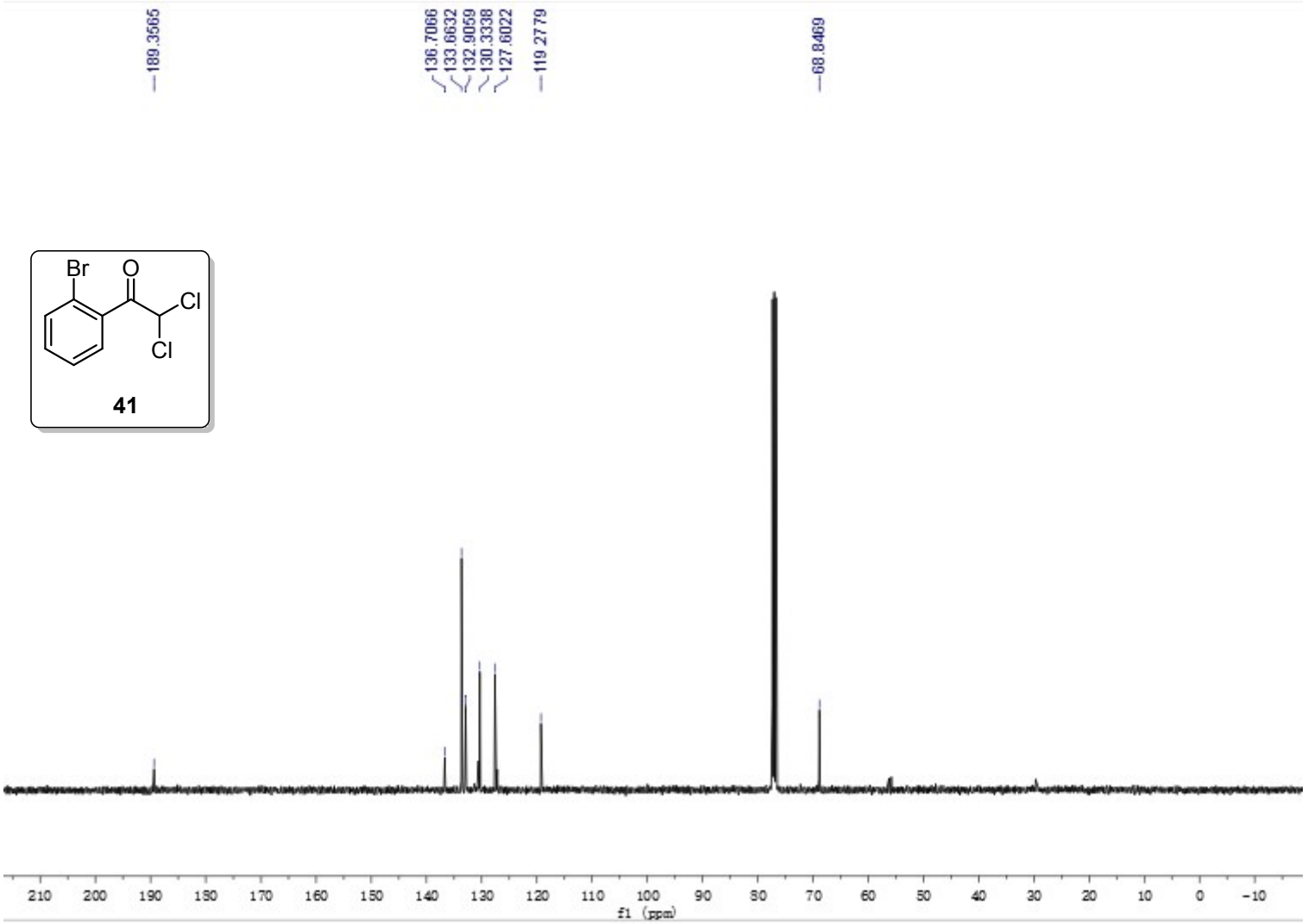
## $^{1}$H NMR of 41

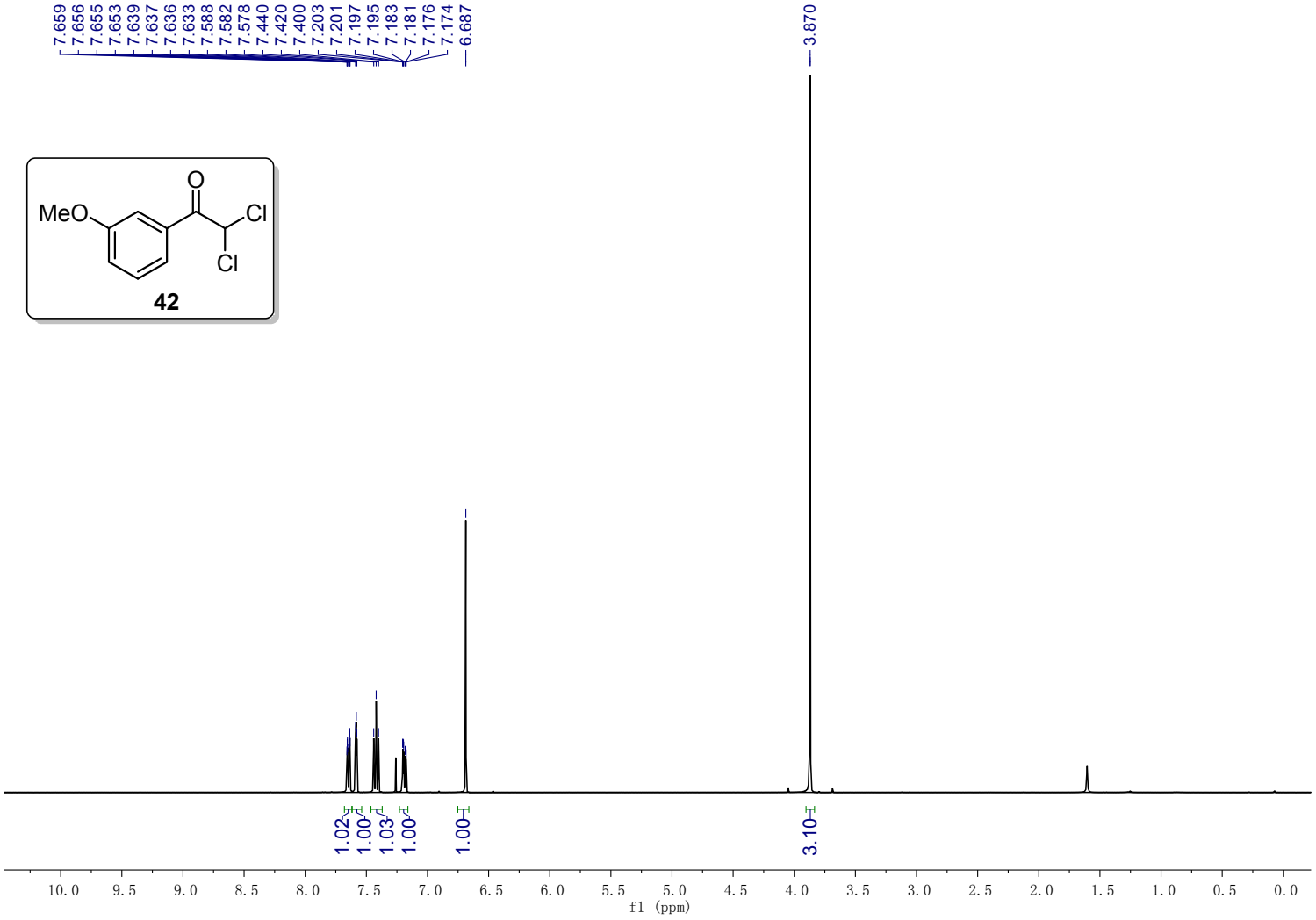

**41**



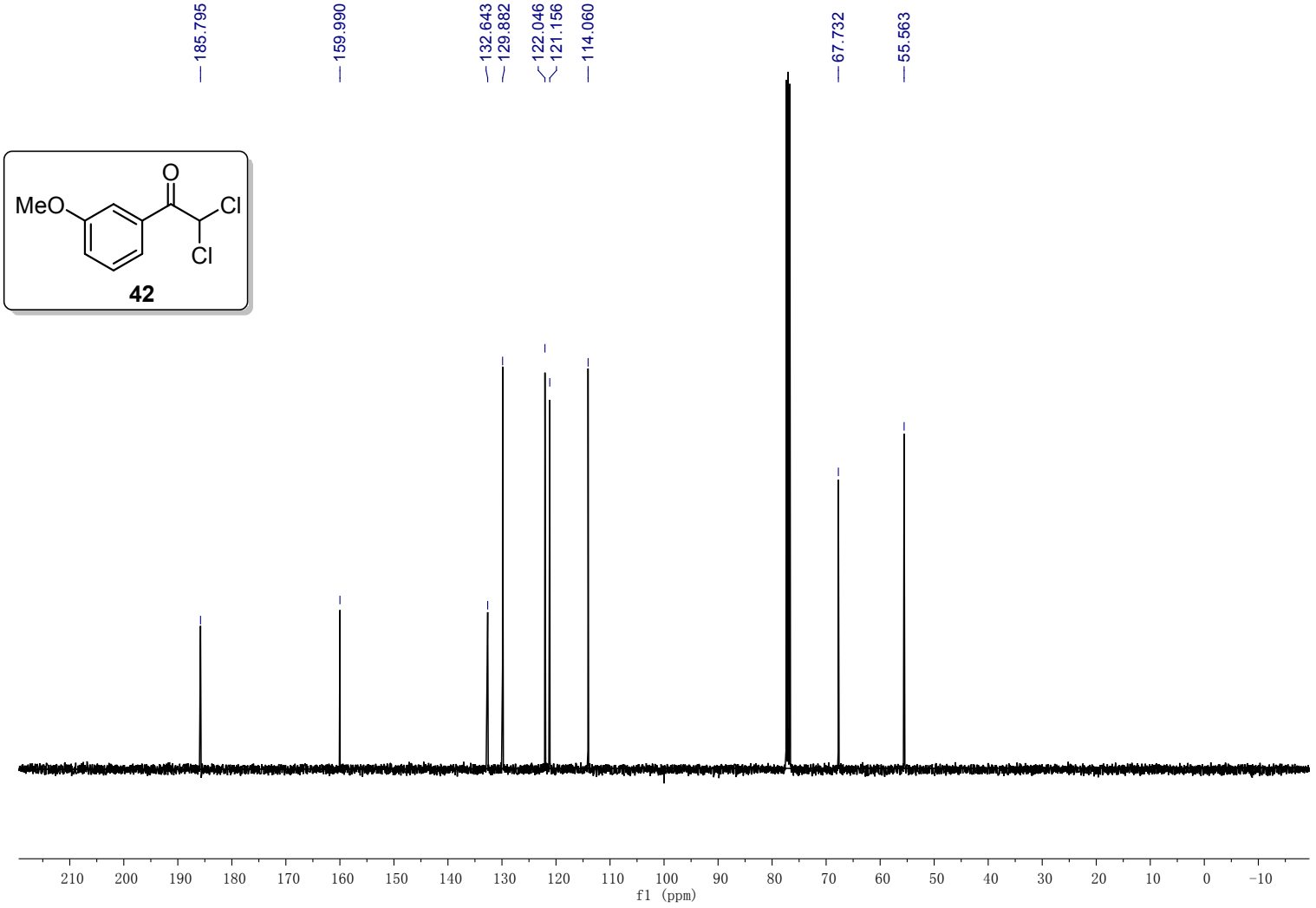
## $^{13}C$ NMR of 41


189.3565
136.7066
133.6632
132.9059
130.3338
127.6022
119.2779
68.8469
Br
O
Cl
Cl
41
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)

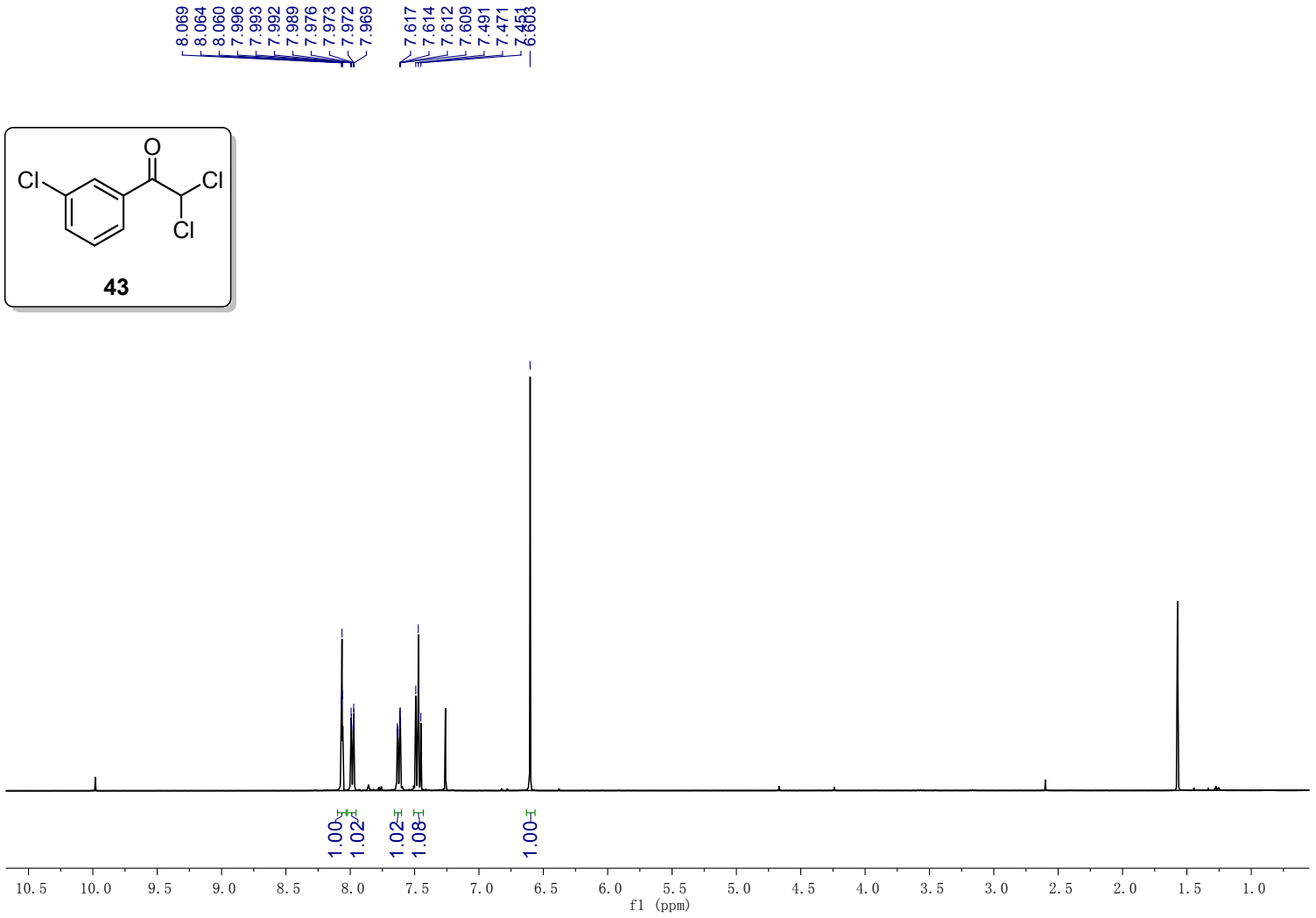
## $^{1}$H NMR of 42


7.659
7.656
7.655
7.653
7.639
7.637
7.636
7.633
7.588
7.582
7.578
7.440
7.420
7.400
7.203
7.201
7.197
7.195
7.183
7.181
7.176
7.174
6.687
3.870
MeO
O
Cl
Cl
42
1.02
1.00
1.03
1.00
1.00
3.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

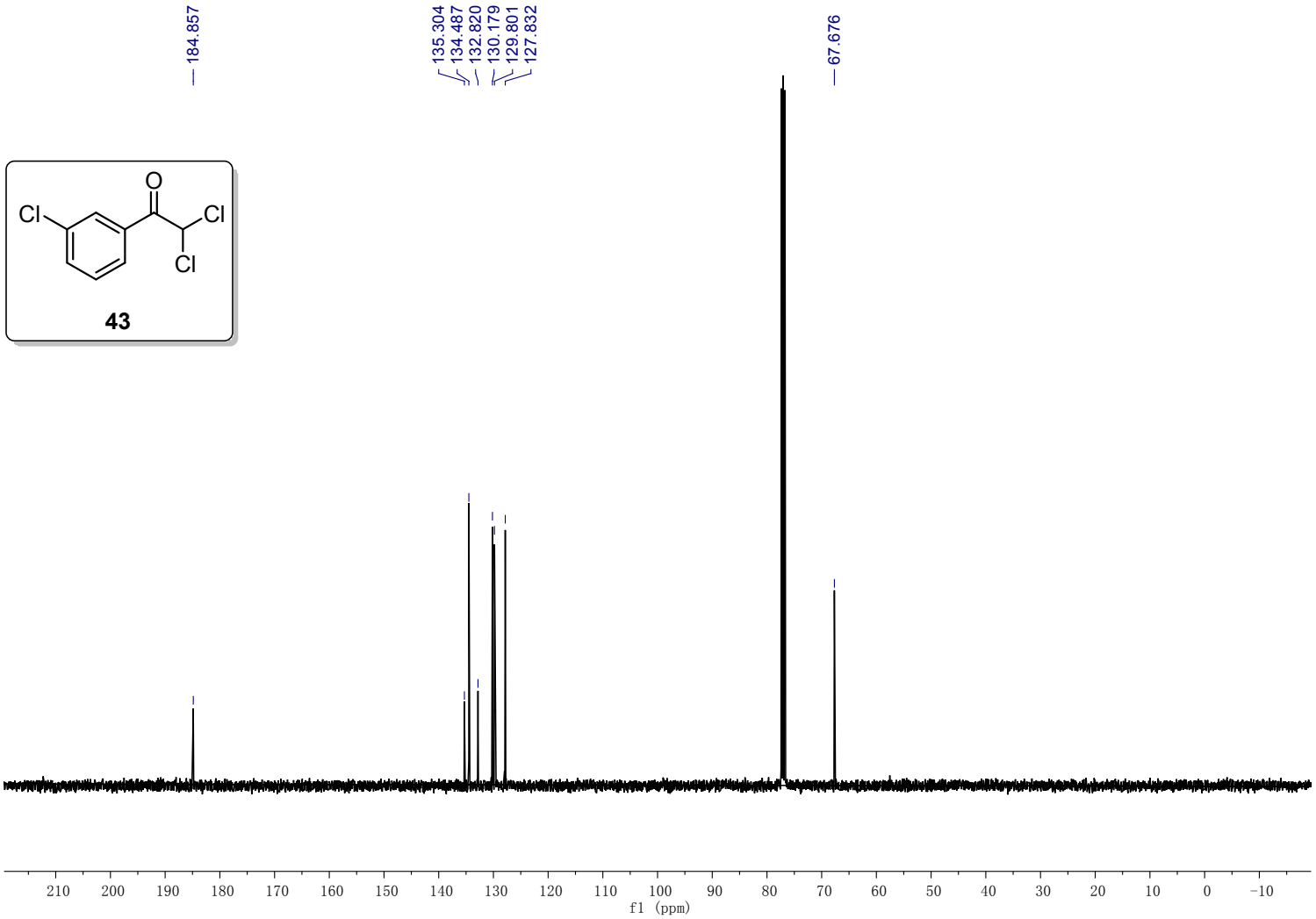
## $^{13}$C NMR of 42


185.795
159.990
132.643
129.882
122.046
121.156
114.060
67.732
55.563
MeO
O
Cl
Cl
42
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)

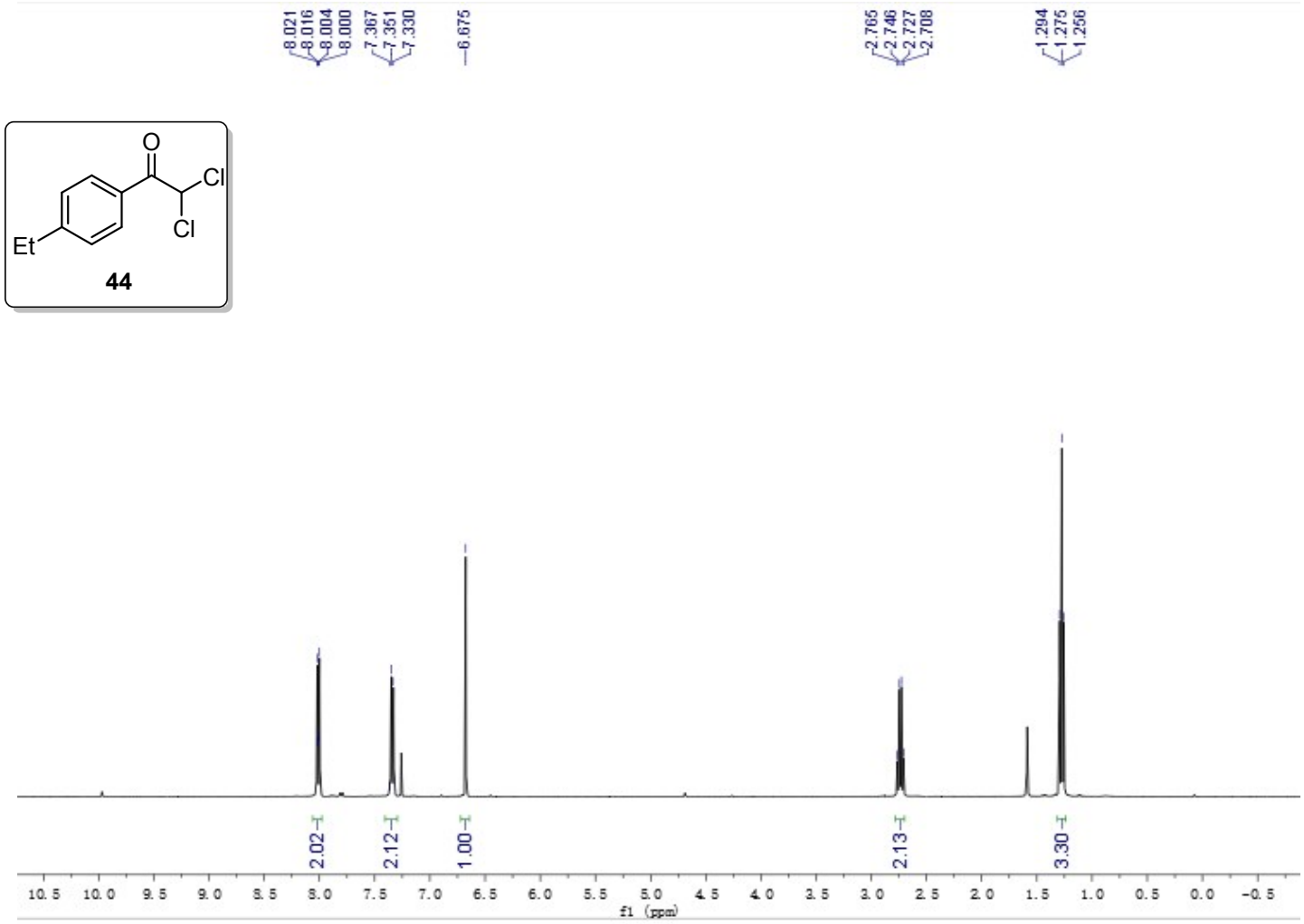
## $^{1}$H NMR of 43


8.069
8.064
8.060
7.996
7.993
7.992
7.989
7.976
7.973
7.972
7.969
7.617
7.614
7.612
7.609
7.491
7.471
7.451
7.443
6.603
O
Cl
Cl
Cl
43
1.00
1.02
1.02
1.08
1.00
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
f1 (ppm)

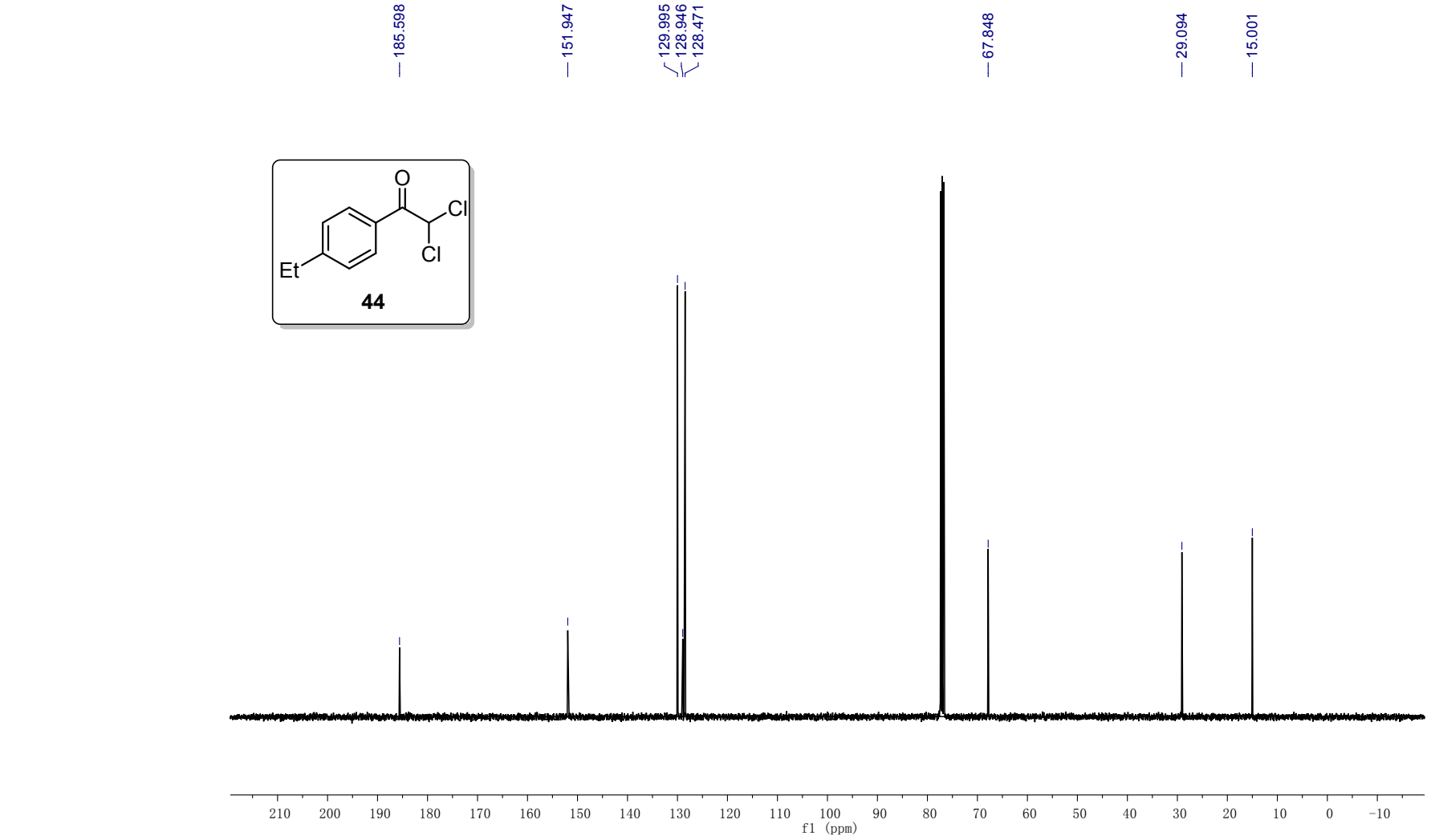
## $^{13}$C NMR of 43


184.857
135.304
134.487
132.820
130.179
129.801
127.832
67.676
Cl
O
Cl
Cl
43
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)

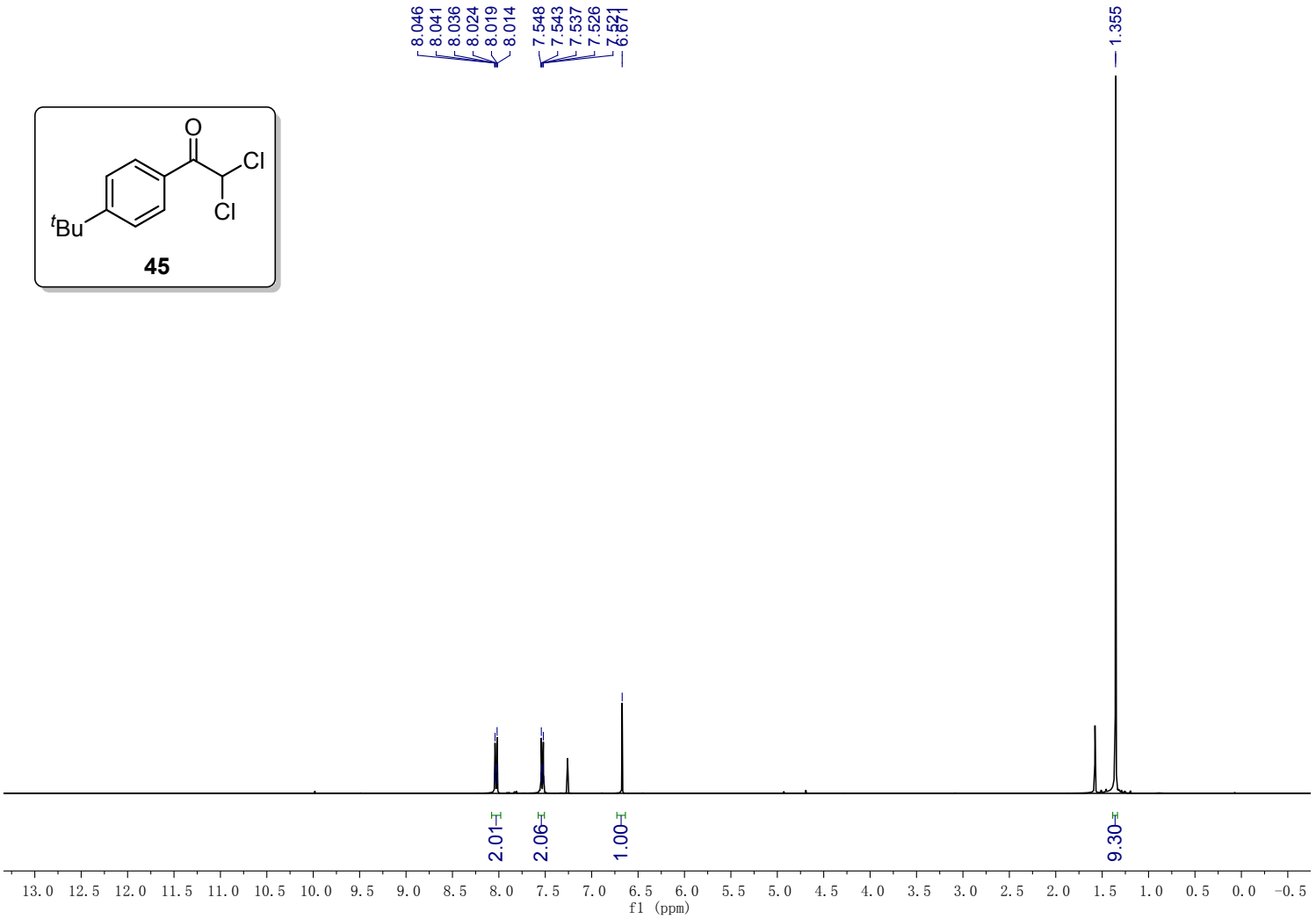
## $^{1}$H NMR of 44


8.021
8.016
8.004
8.000
7.367
7.351
7.330
6.675
2.765
2.746
2.727
2.708
1.294
1.275
1.256
O
Cl
Cl
Et
44
2.02
2.12
1.00
2.13
3.30
f1 (ppm)

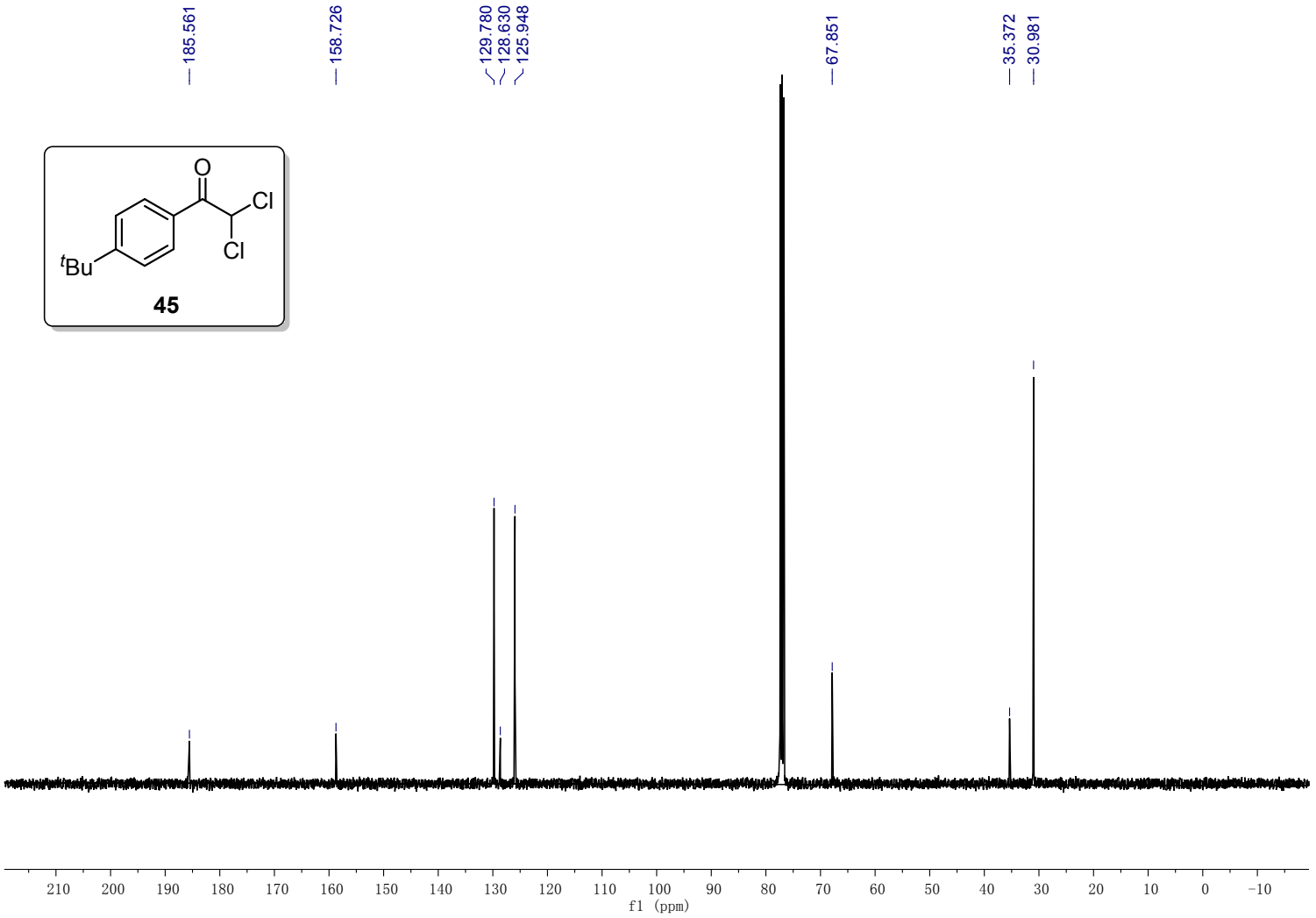
## $^{13}$C NMR of 44


185.598
151.947
129.995
128.946
128.471
67.848
29.094
15.001
O
Cl
Cl
Et
44
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)

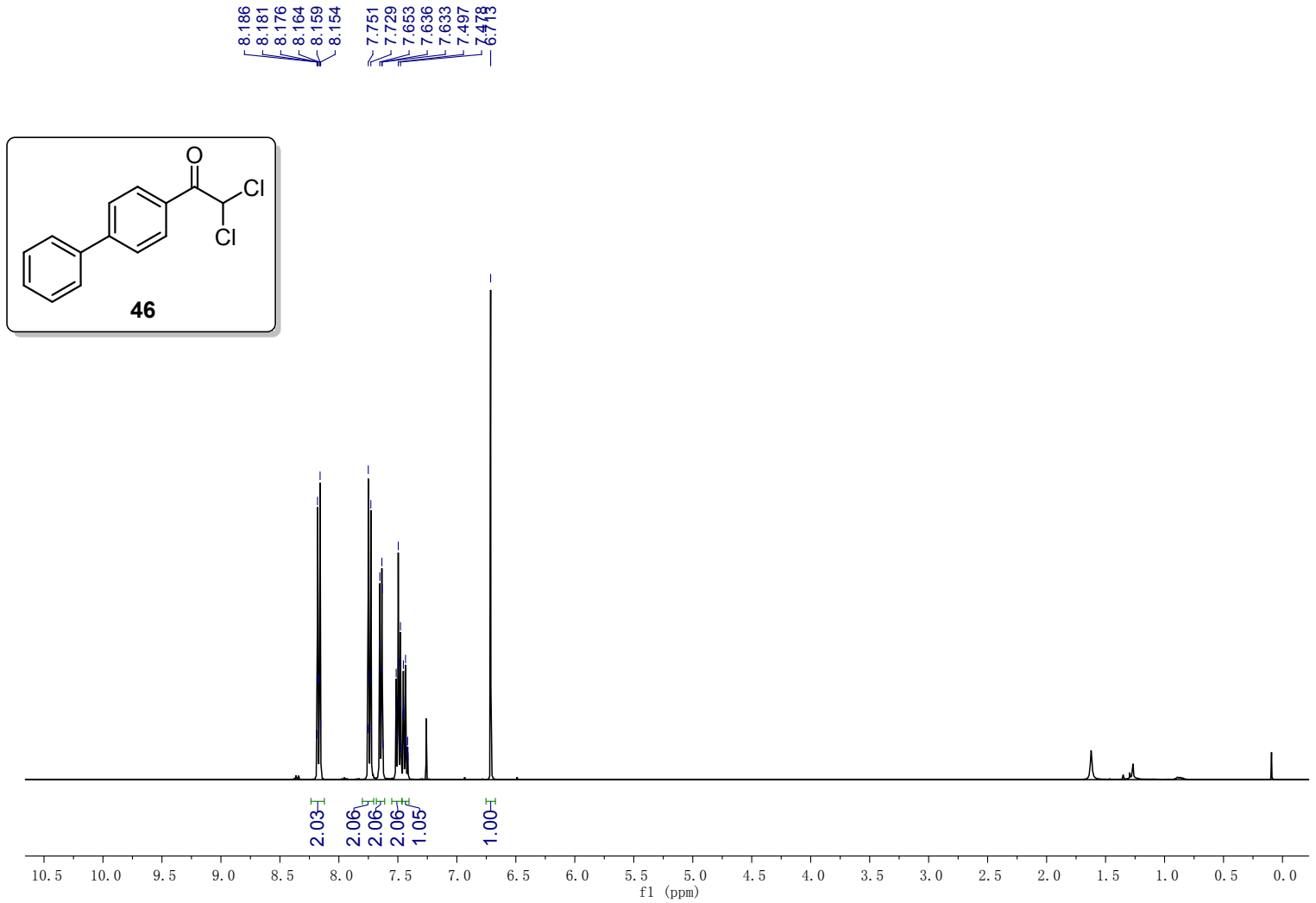
## $^{1}$H NMR of 45


8.046
8.041
8.036
8.024
8.019
8.014
7.548
7.543
7.537
7.526
7.521
6.871
1.355
O
Cl
Cl
tBu
45
2.01
2.06
1.00
9.30
13.0 12.5 12.0 11.5 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
f1 (ppm)

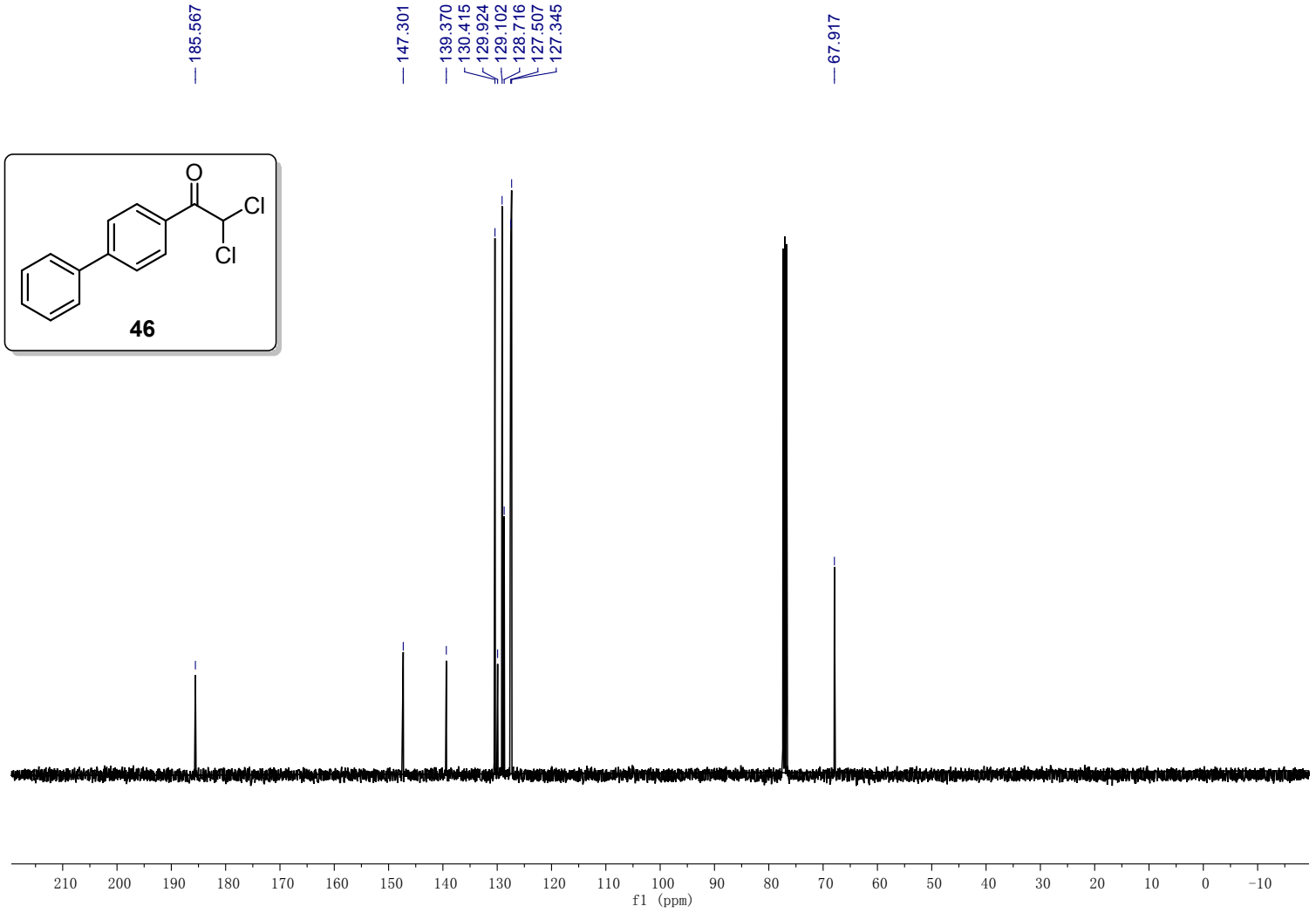
## $^{13}$C NMR of 45


185.561
158.726
129.780
128.630
125.948
67.851
35.372
30.981
O
Cl
Cl
tBu
45
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)

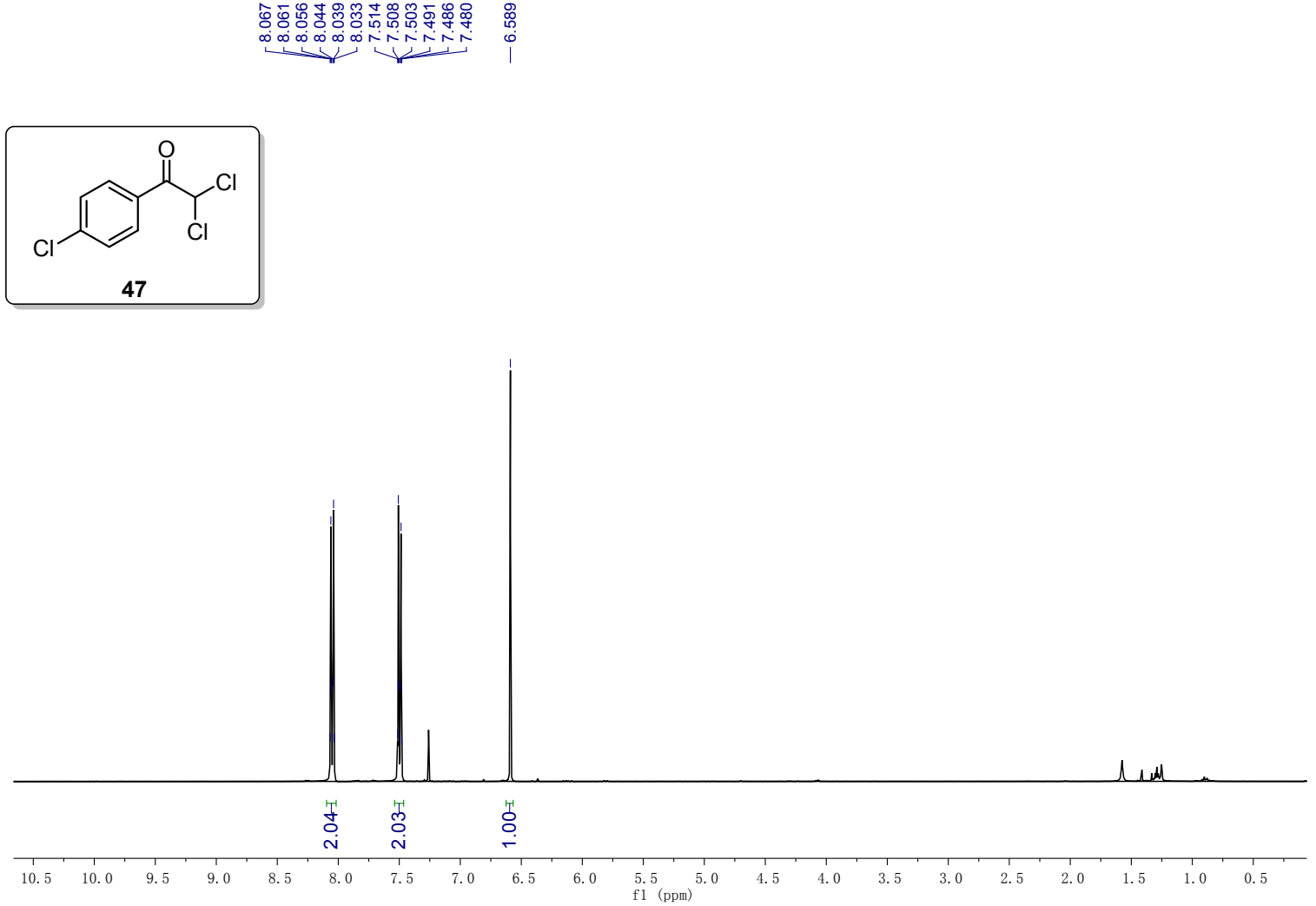
## $^{1}$H NMR of 46


8.186
8.181
8.176
8.164
8.159
8.154
7.751
7.729
7.653
7.636
7.633
7.497
7.478
7.473
O
Cl
Cl
46
2.03
2.06
2.06
2.06
1.05
1.00
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
f1 (ppm)

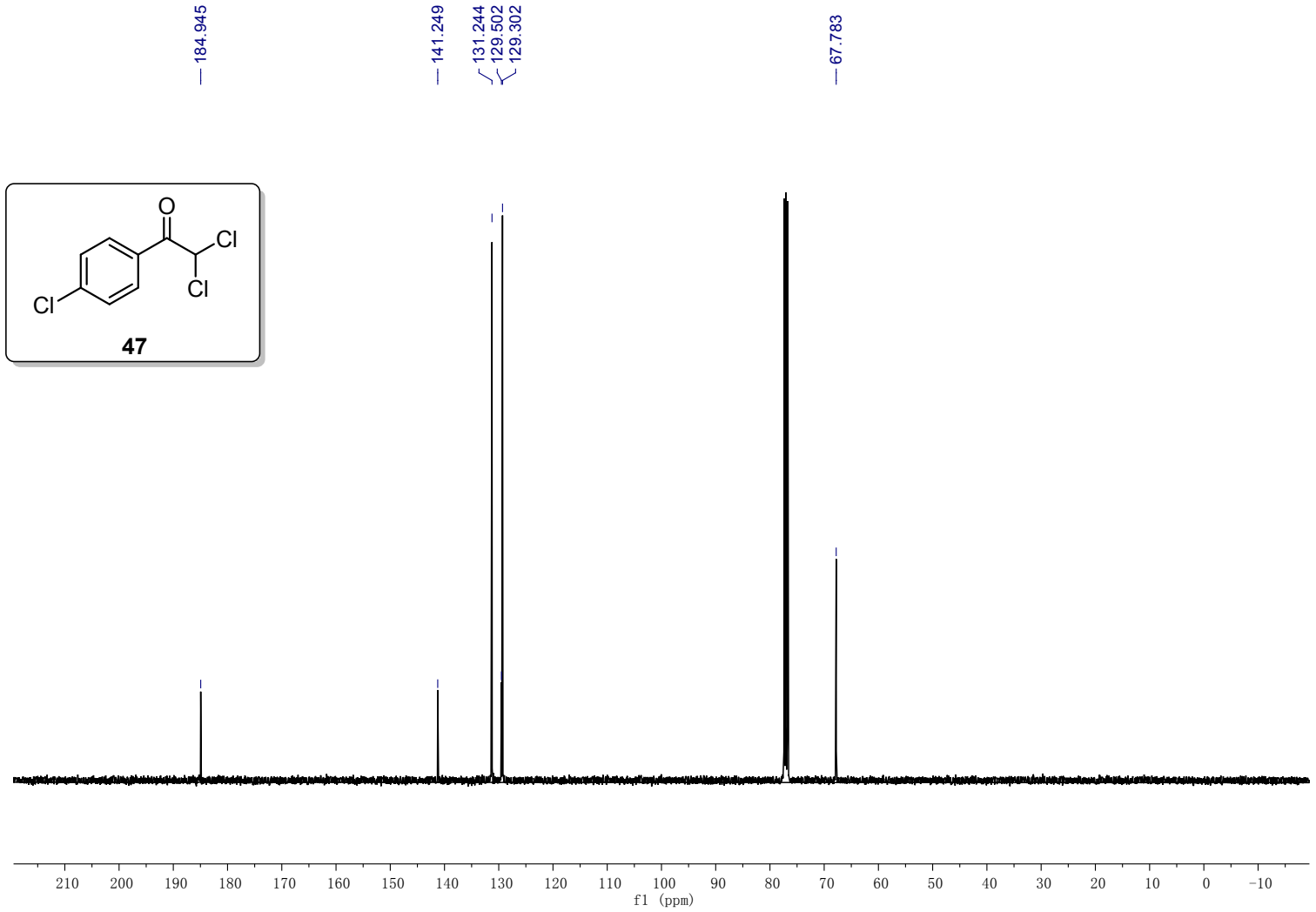
## $^{13}$C NMR of 46


185.567
147.301
139.370
130.415
129.924
129.102
128.716
127.507
127.345
67.917
O
Cl
Cl
46
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)

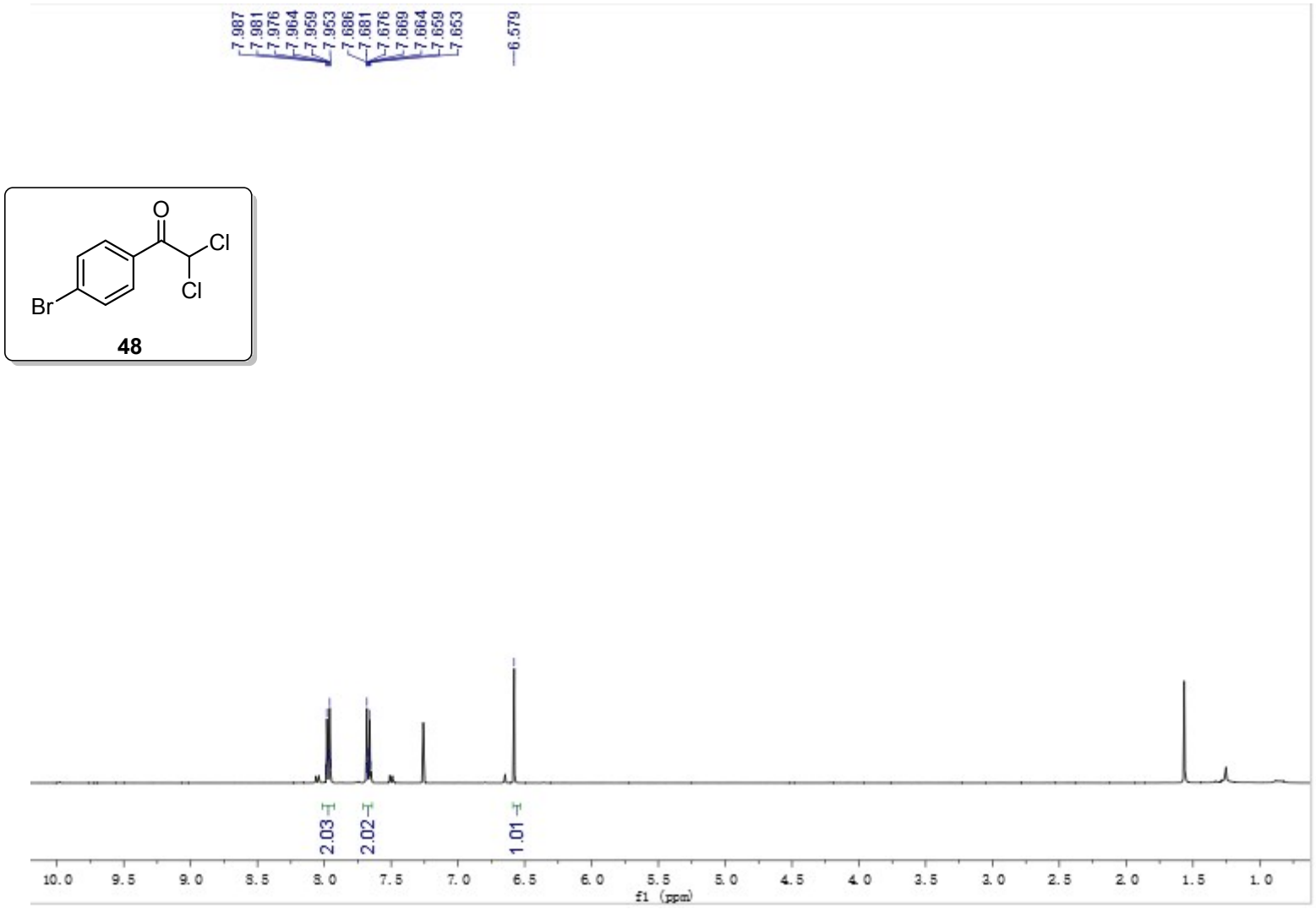
## $^{1}$H NMR of 47


8.067
8.061
8.056
8.044
8.039
8.033
7.514
7.508
7.503
7.491
7.486
7.480
6.589
O
Cl
Cl
Cl
47
2.04
2.03
1.00
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
f1 (ppm)

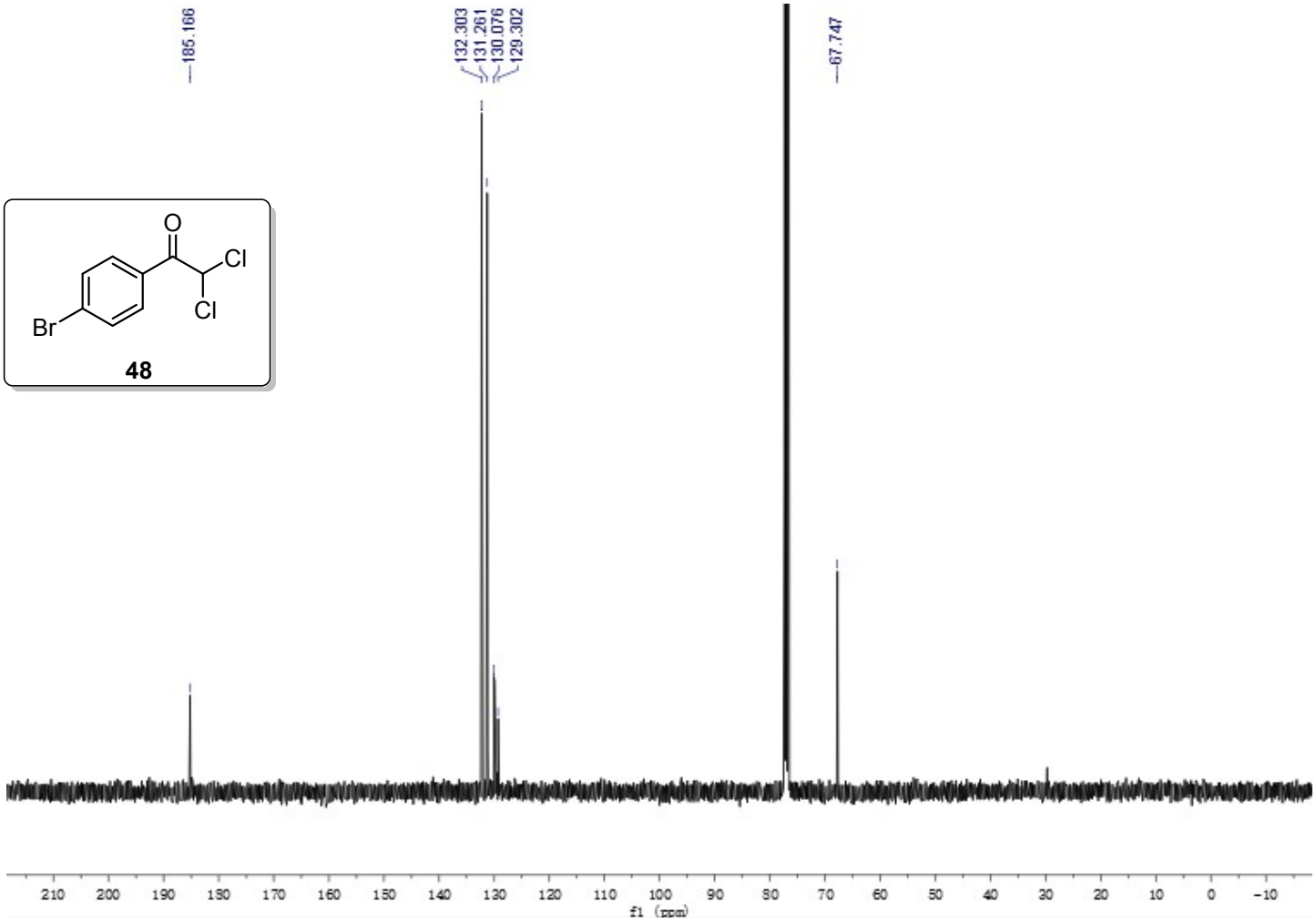
## $^{13}$C NMR of 47


184.945
141.249
131.244
129.502
129.302
67.783
O
Cl
Cl
Cl
47
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)

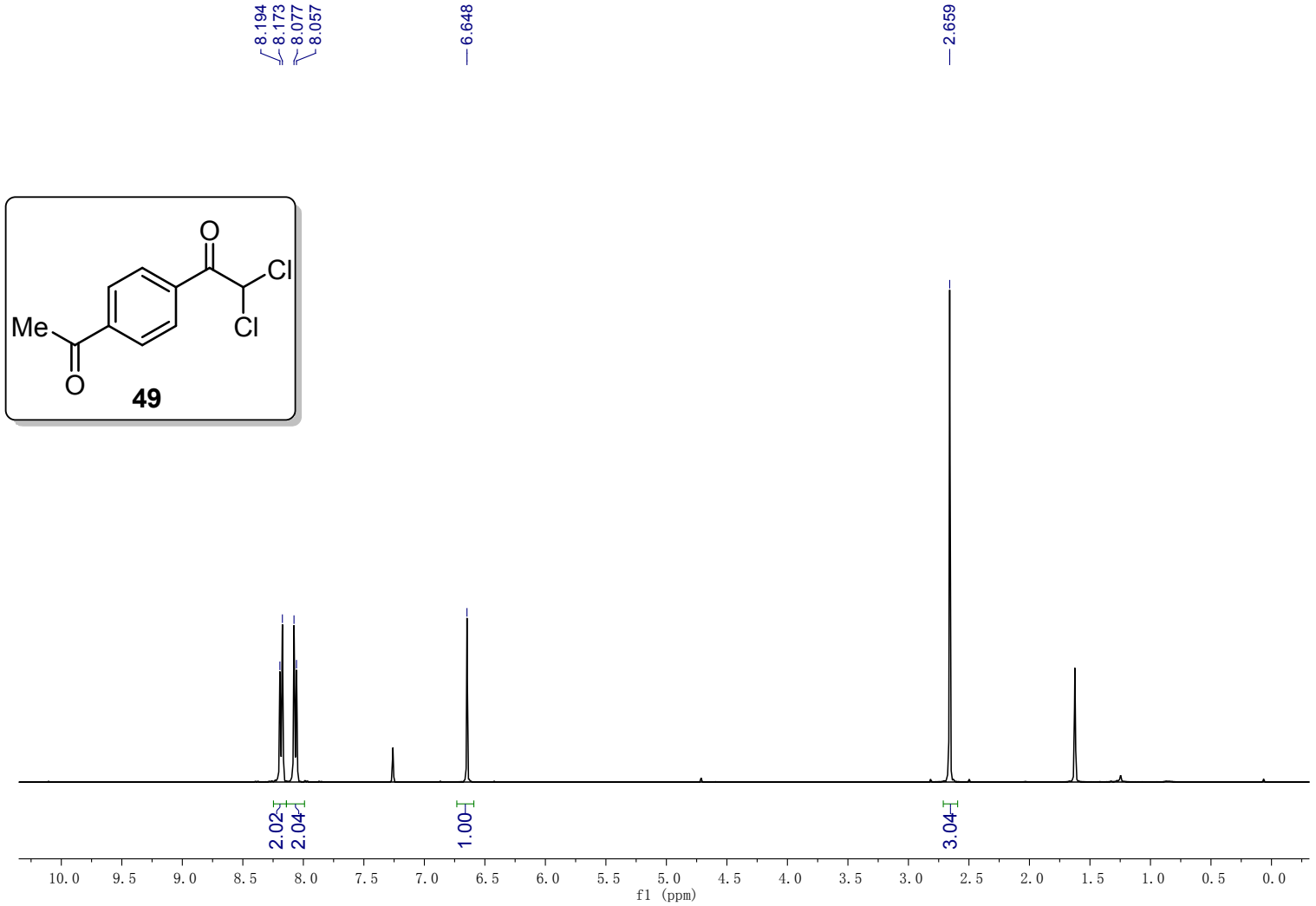
## $^{1}$H NMR of 48


7.987
7.981
7.976
7.964
7.959
7.953
7.686
7.681
7.676
7.669
7.664
7.659
7.653
6.579
O
Cl
Cl
Br
48
2.03
2.02
1.01
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
f1 (ppm)

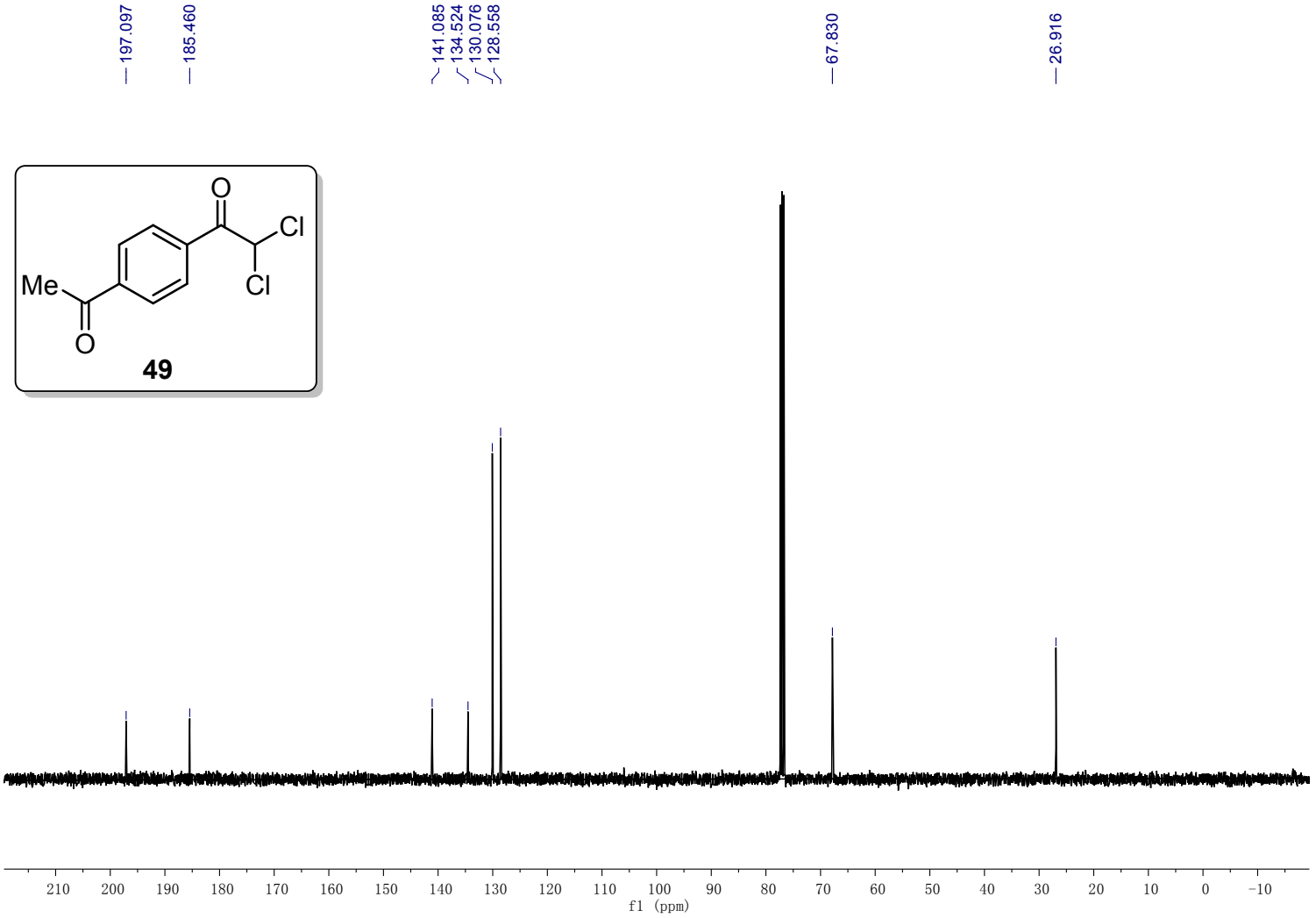
**$^{13}$C NMR of 48**


185.166
132.303
131.261
130.076
129.302
67.747
O
Cl
Cl
Br
48
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)

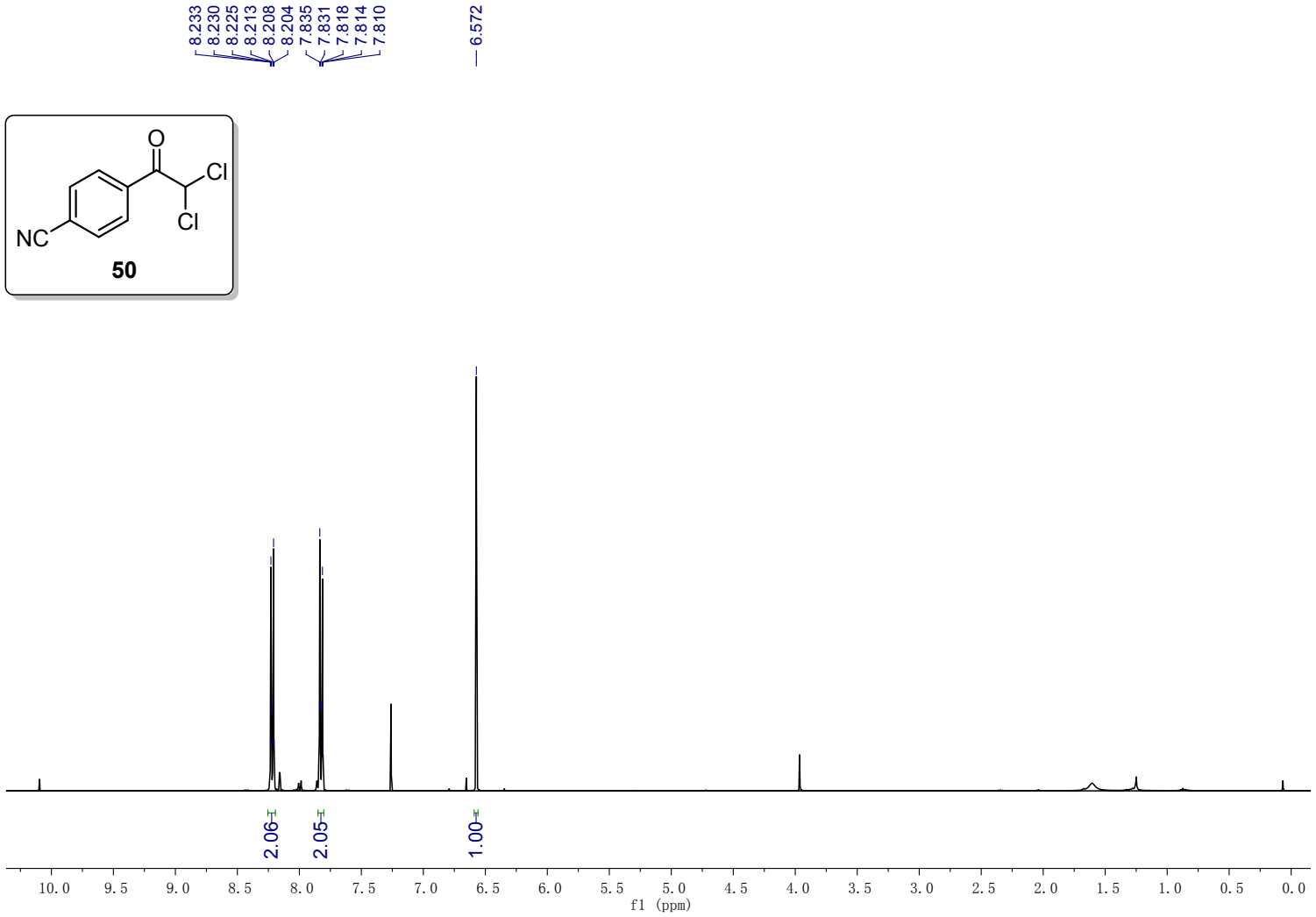
## $^{1}$H NMR of 49


8.194
8.173
8.077
8.057
6.648
2.659
O
Cl
Cl
Me
O
49
2.02
2.04
1.00
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

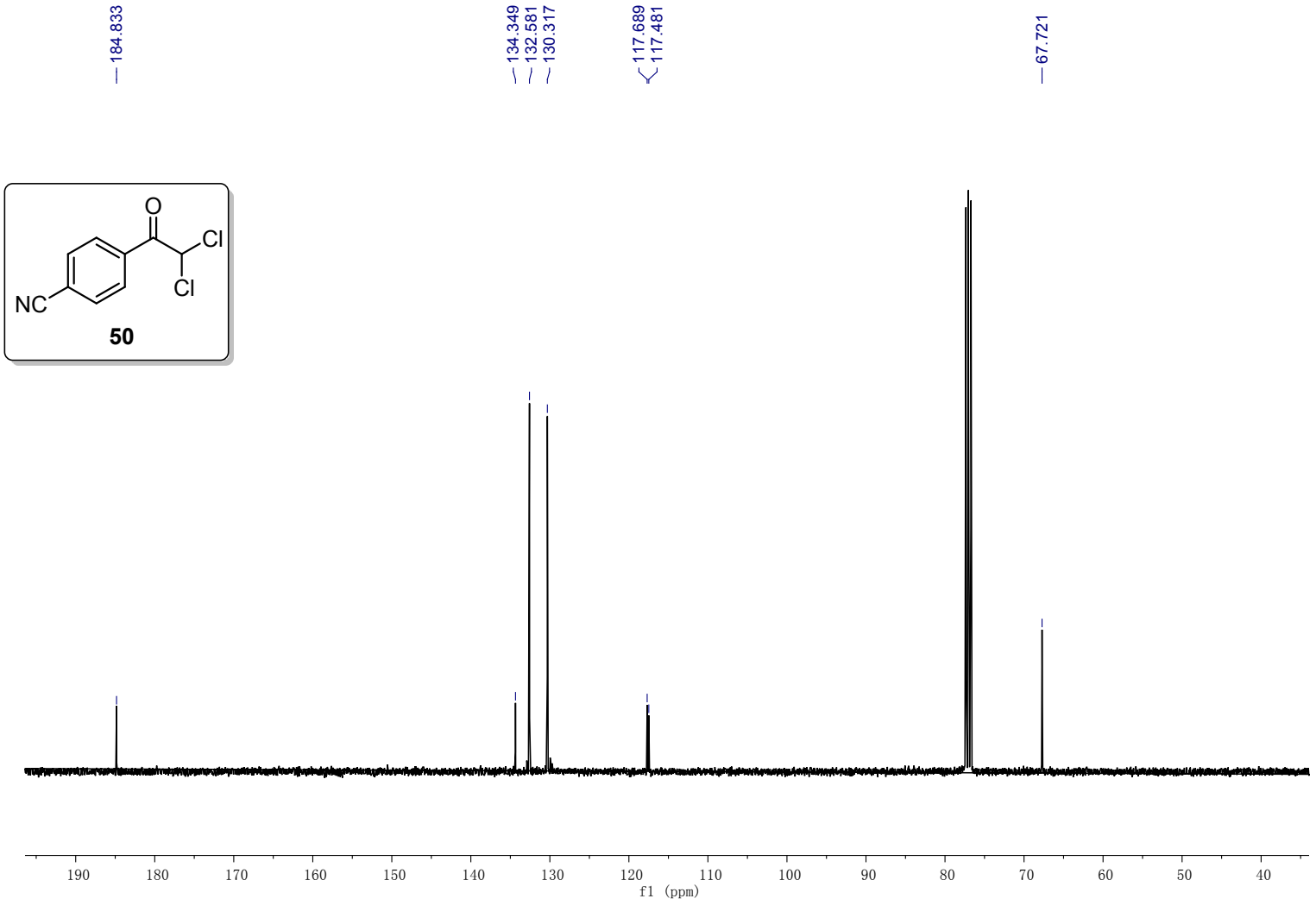
## $^{13}$C NMR of 49


197.097
185.460
141.085
134.524
130.076
128.558
67.830
26.916
O
Cl
Cl
Me
O
49
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)

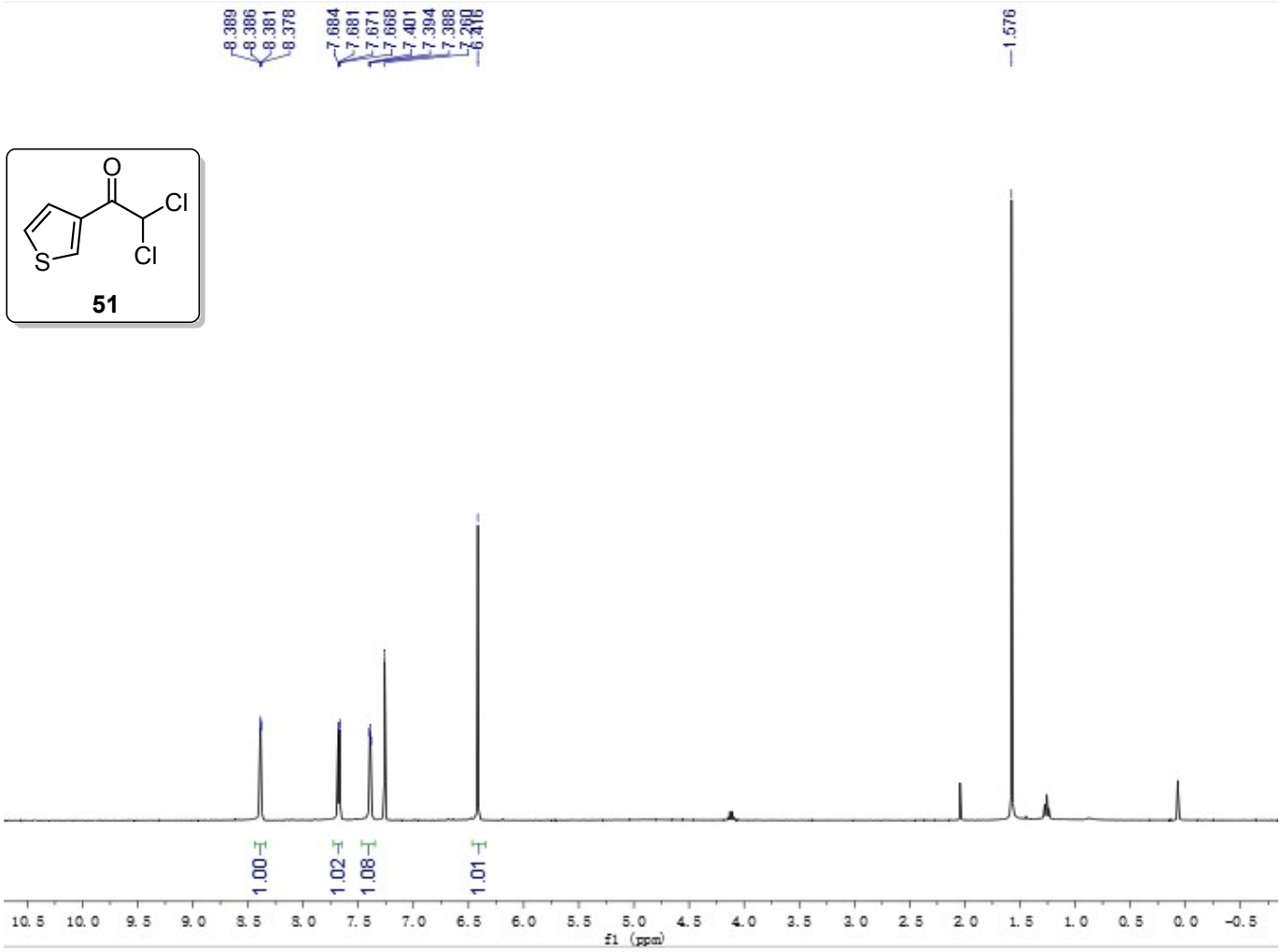
## $^{1}$H NMR of 50


8.233
8.230
8.225
8.213
8.208
8.204
7.835
7.831
7.818
7.814
7.810
6.572
O
Cl
Cl
NC
50
2.06
2.05
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

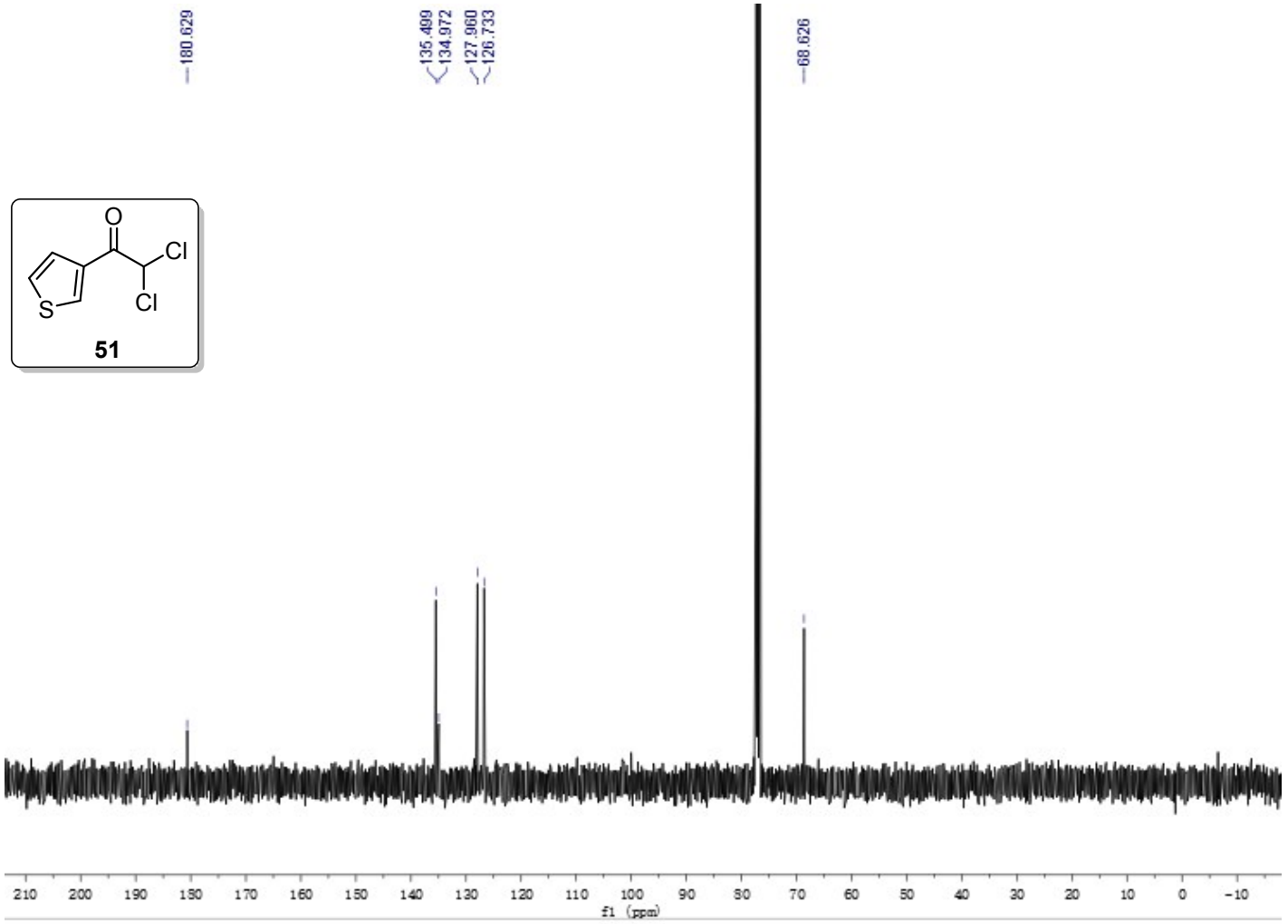
## $^{13}$C NMR of 50


184.833
134.349
132.581
130.317
117.689
117.481
67.721
O
Cl
Cl
NC
50
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
f1 (ppm)

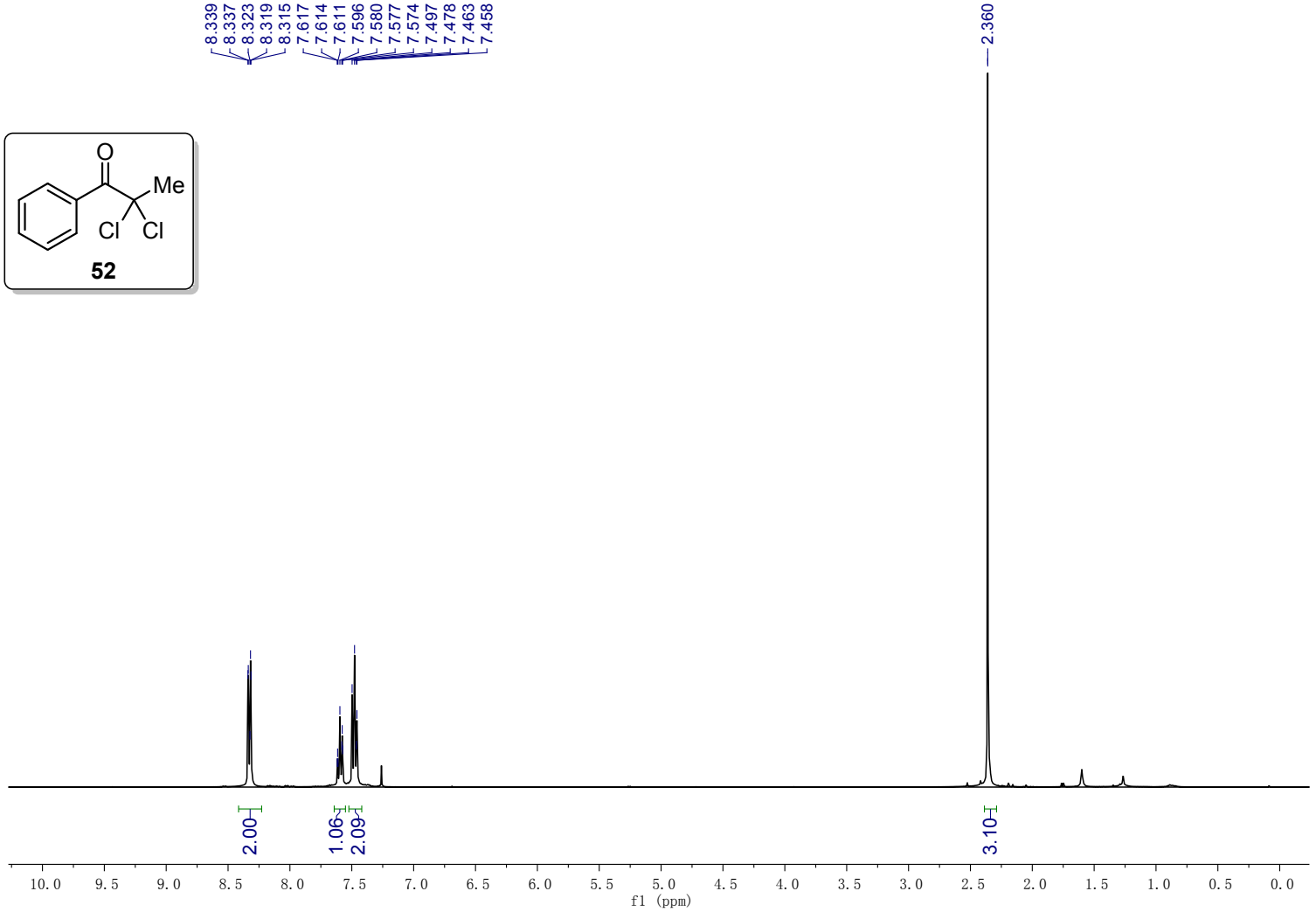
## $^{1}$H NMR of 51


8.389
8.386
8.381
8.378
7.684
7.681
7.671
7.668
7.401
7.394
7.388
7.260
1.576
O
Cl
Cl
S
51
1.00
1.02
1.08
1.01
f1 (ppm)

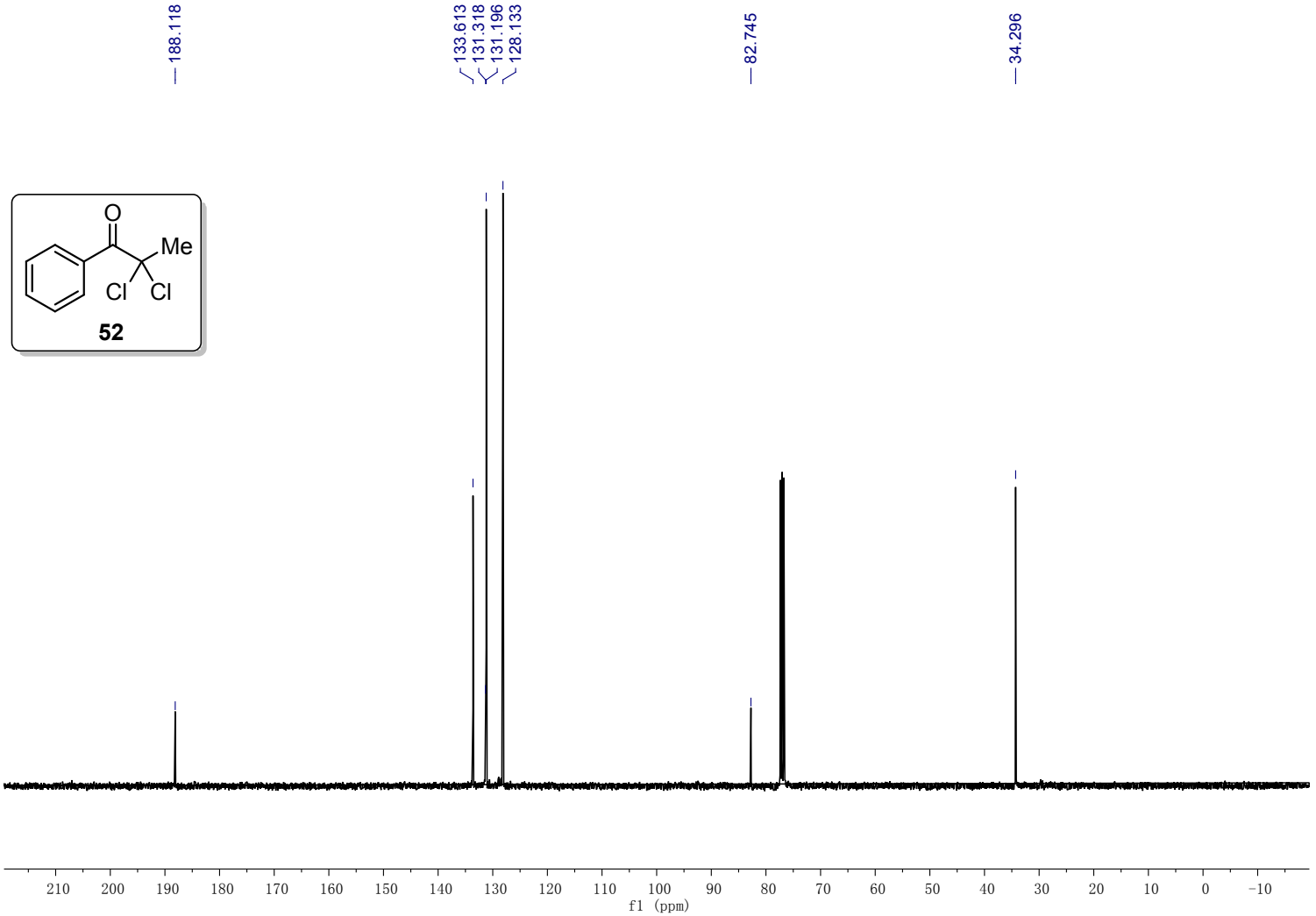
**$^{13}$C NMR of 51**


180.629
135.499
134.972
127.960
126.733
68.626
O
Cl
Cl
S
51
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)

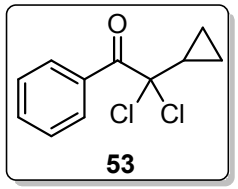
## $^{1}$H NMR of 52


8.339
8.337
8.323
8.319
8.315
7.617
7.614
7.611
7.596
7.580
7.577
7.574
7.497
7.478
7.463
7.458
2.360
O
Me
Cl
Cl
52
2.00
1.06
2.09
3.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

## $^{13}$C NMR of 52

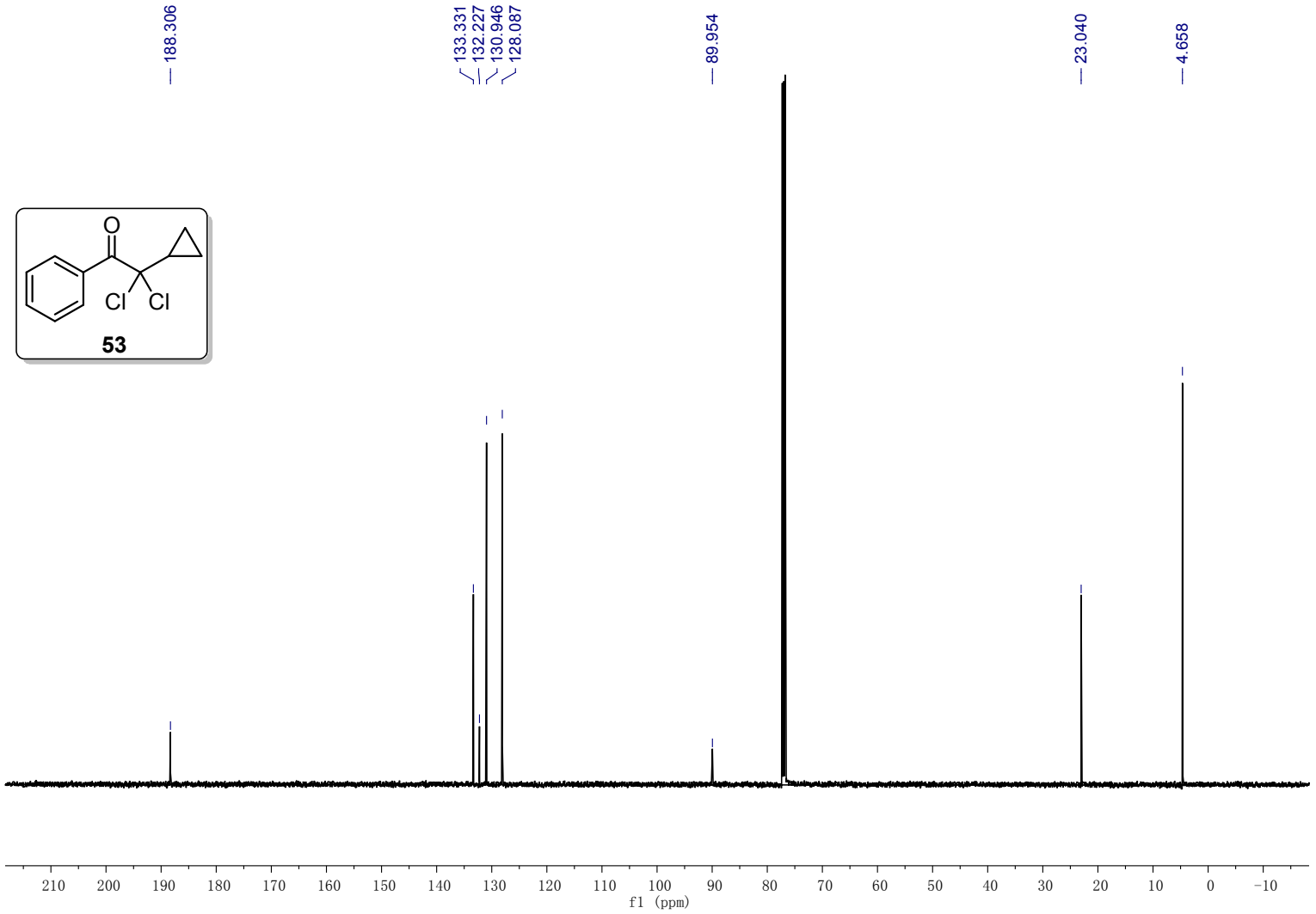

188.118
133.613
131.318
131.196
128.133
82.745
34.296
O
Me
Cl
Cl
52
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

## $^{1}$H NMR of 53

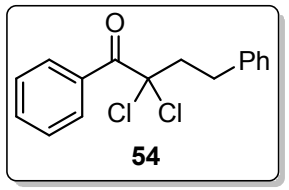



**53**

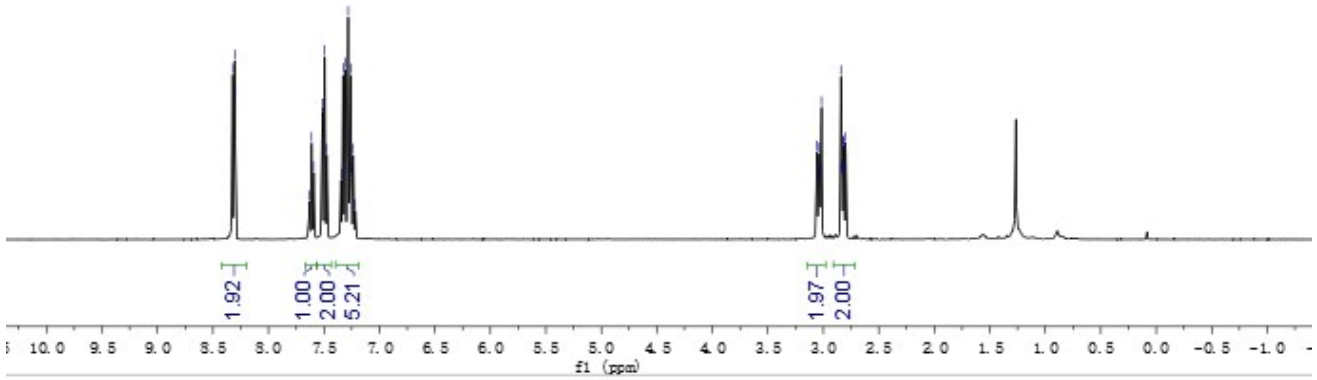
## $^{13}$C NMR of 53


188.306
133.331
132.227
130.946
128.087
89.954
23.040
4.658
O
Cl
Cl
53
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)

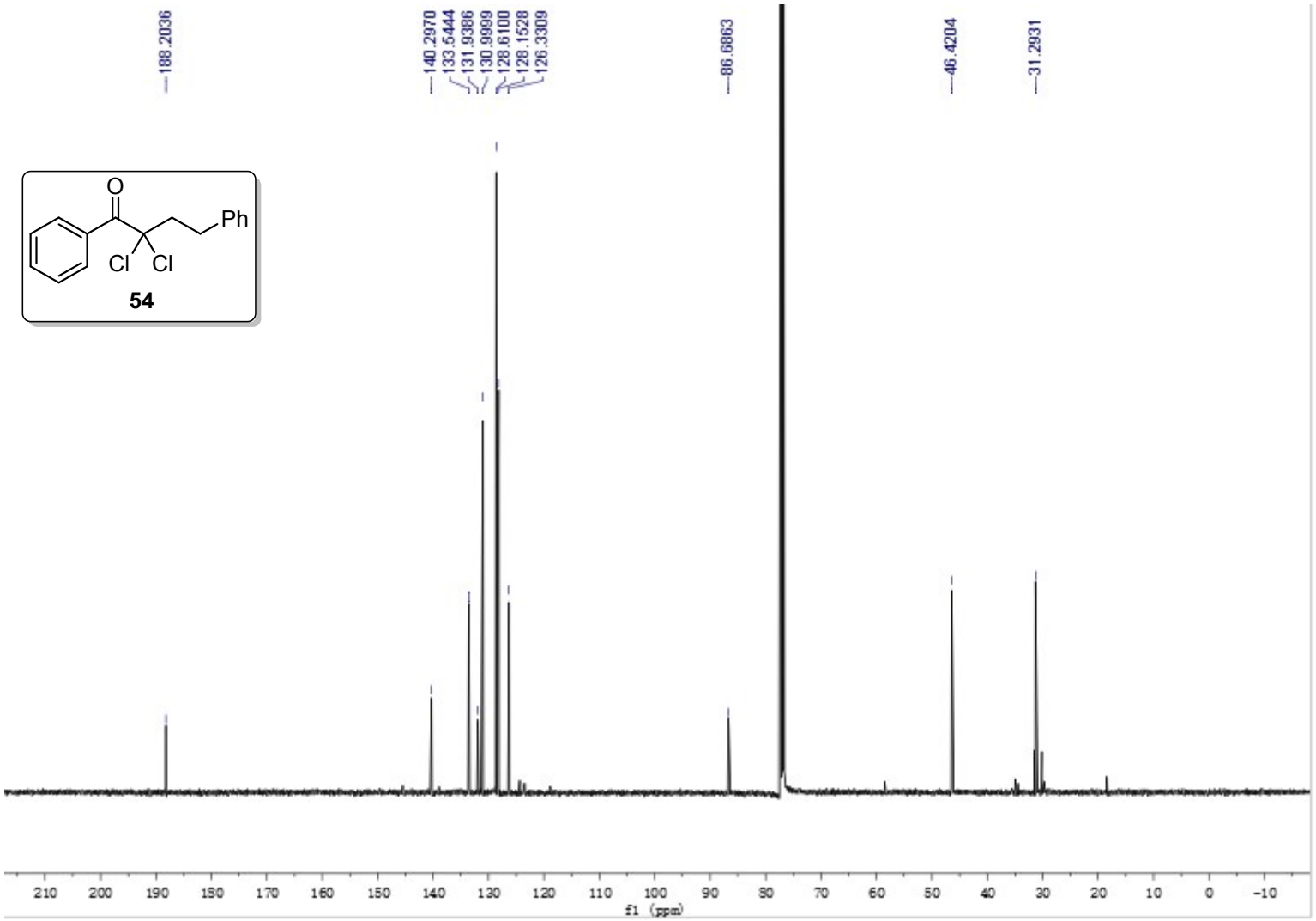
## $^{1}$H NMR of 54

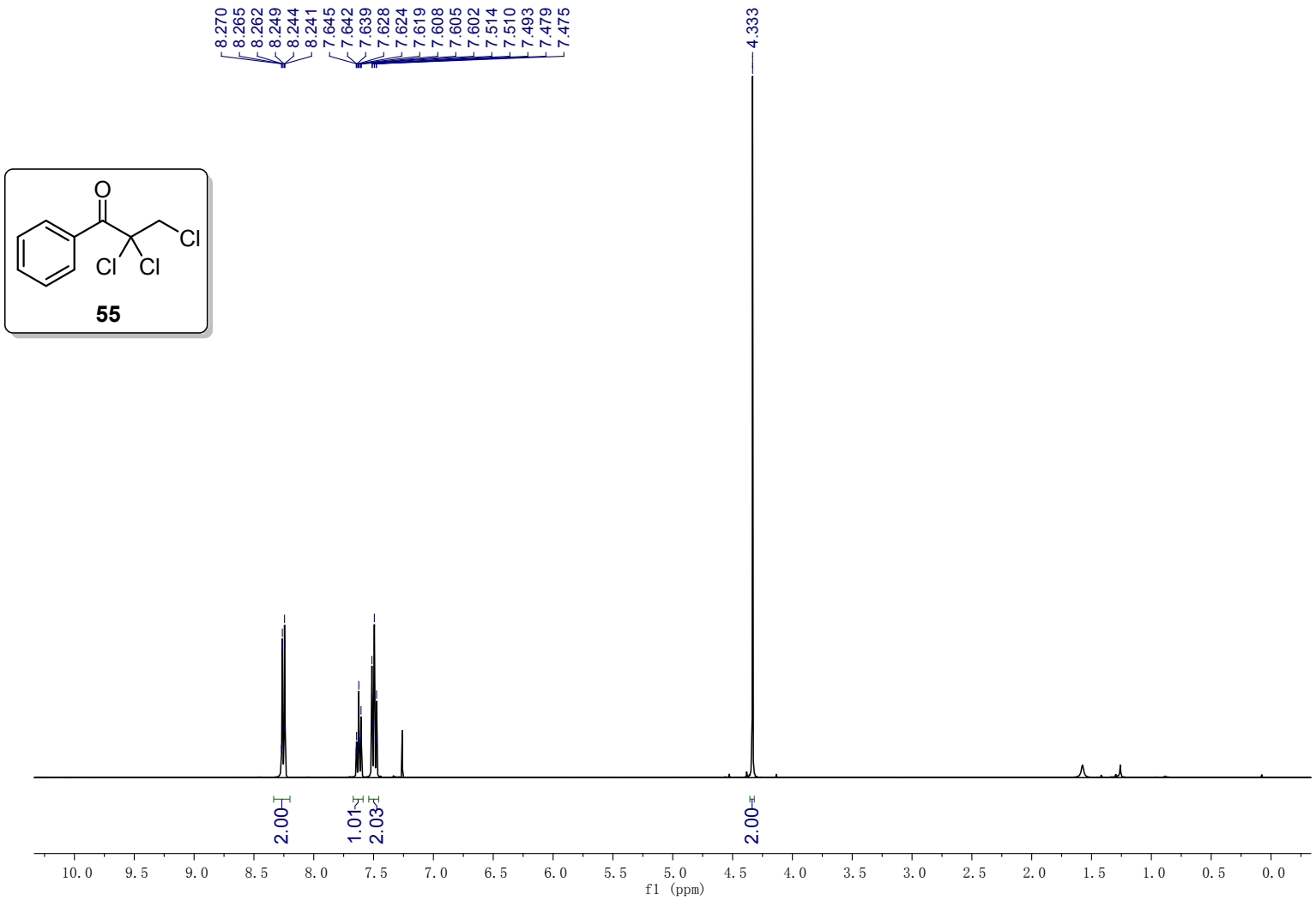

**54**



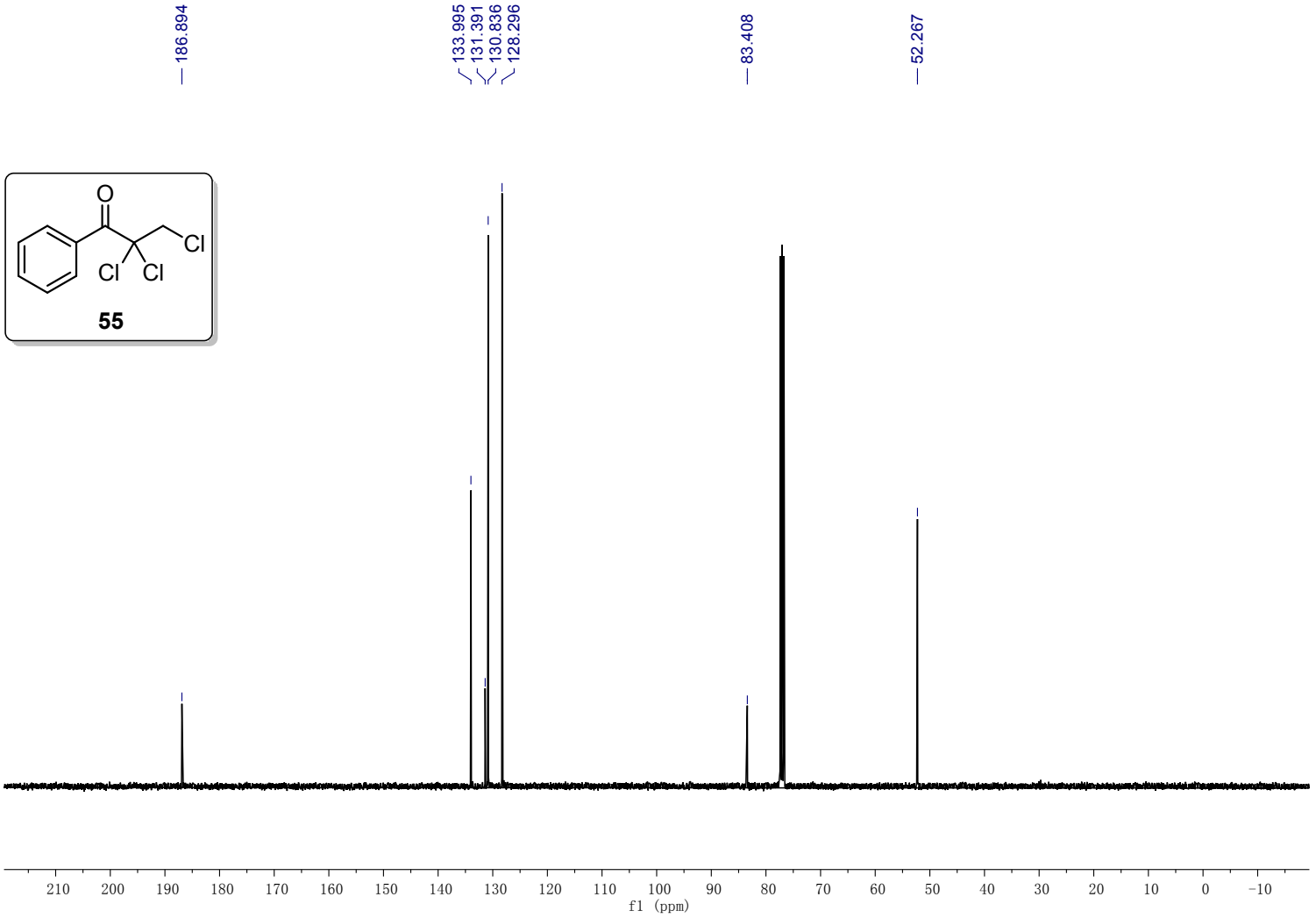
**$^{13}$C NMR of 54**


188.2036
140.2970
133.5444
131.9386
130.9999
128.6100
128.1528
126.3309
86.6863
46.4204
31.2931
O
Ph
Cl
Cl
54
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)

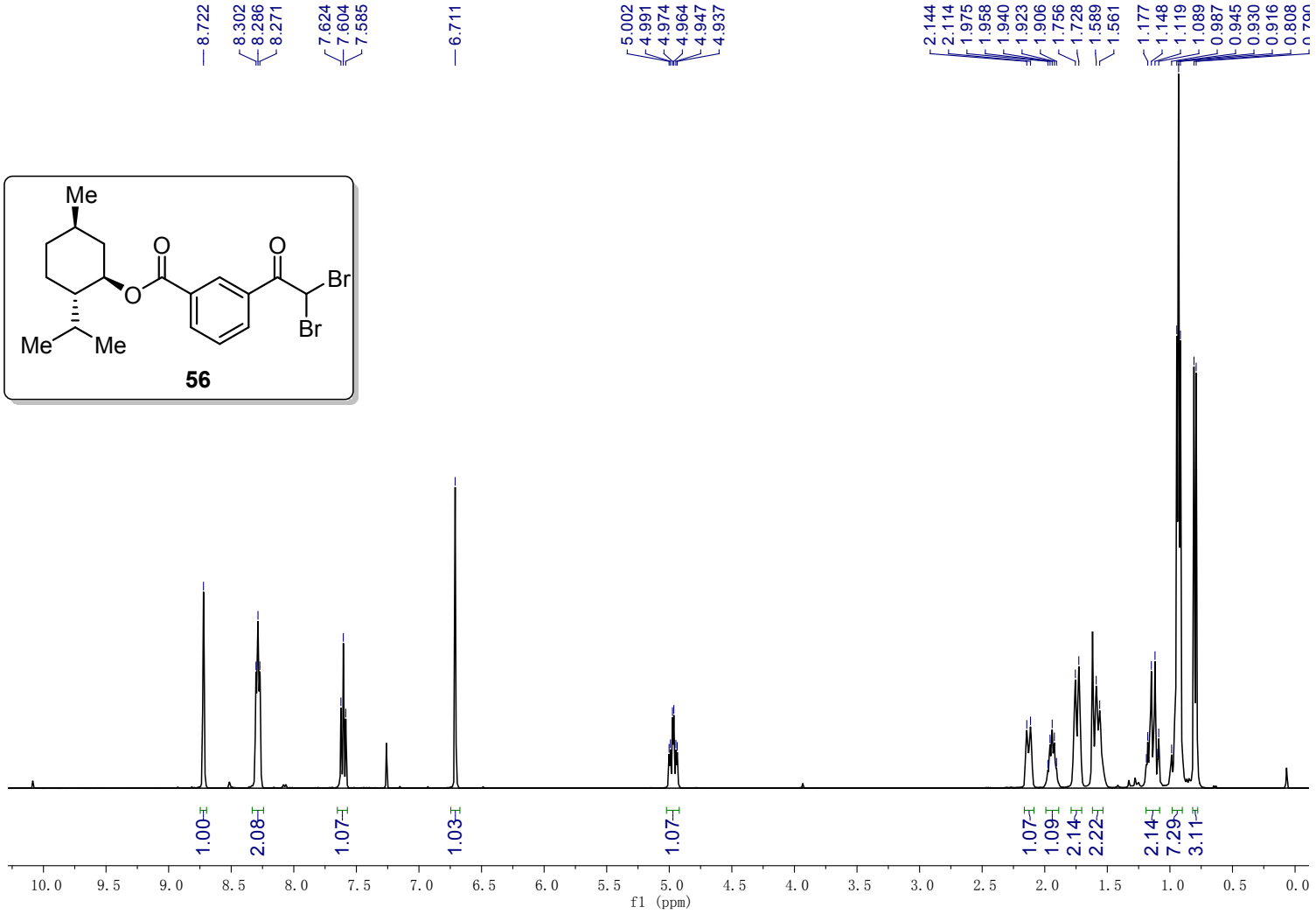
## $^{1}$H NMR of 55


8.270
8.265
8.262
8.249
8.244
8.241
7.645
7.642
7.639
7.628
7.624
7.619
7.608
7.605
7.602
7.514
7.510
7.493
7.479
7.475
4.333
O
Cl
Cl
Cl
55
2.00
1.01
2.03
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

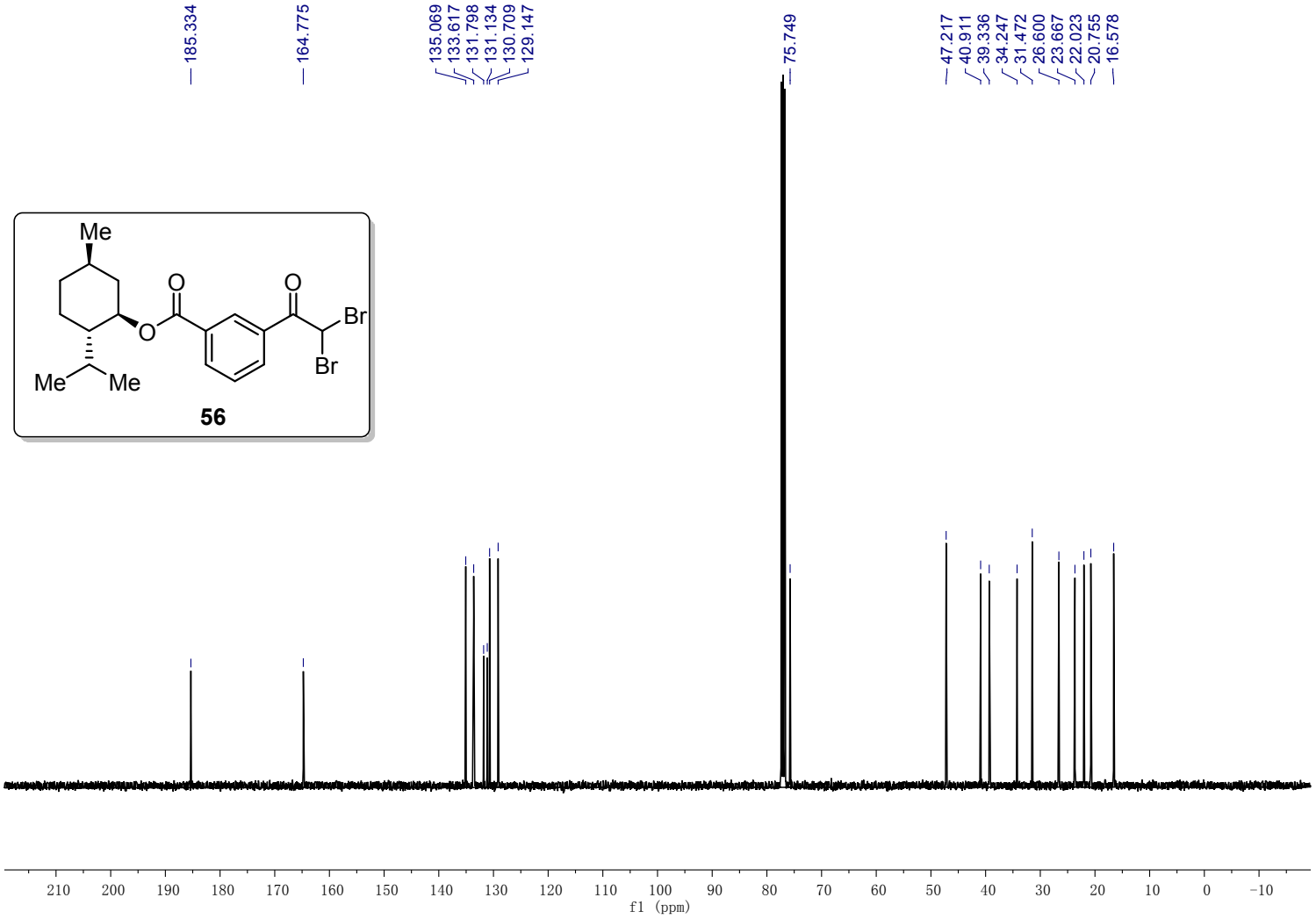
## $^{13}$C NMR of 55


186.894
133.995
131.391
130.836
128.296
83.408
52.267
O
Cl
Cl
Cl
55
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)

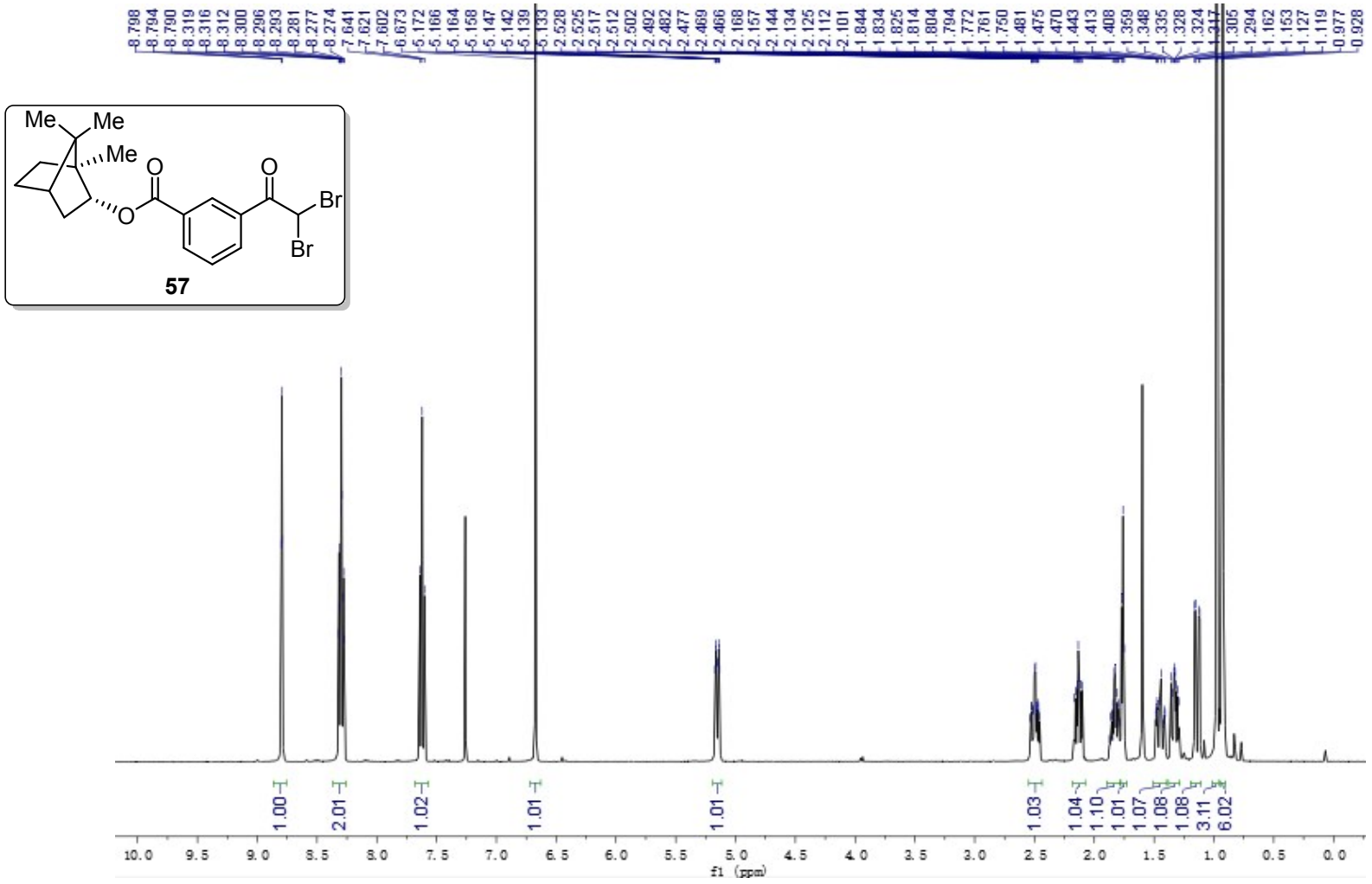
## $^{1}$H NMR of 56


8.722
8.302
8.286
8.271
7.624
7.604
7.585
6.711
5.002
4.991
4.974
4.964
4.947
4.937
2.144
2.114
1.975
1.958
1.940
1.923
1.906
1.756
1.728
1.589
1.561
1.177
1.148
1.119
1.089
0.987
0.945
0.930
0.916
0.808
Me
O
O
O
Br
Br
Me
Me
56
1.00
2.08
1.07
1.03
1.07
1.07
1.09
2.14
2.22
2.14
7.29
3.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

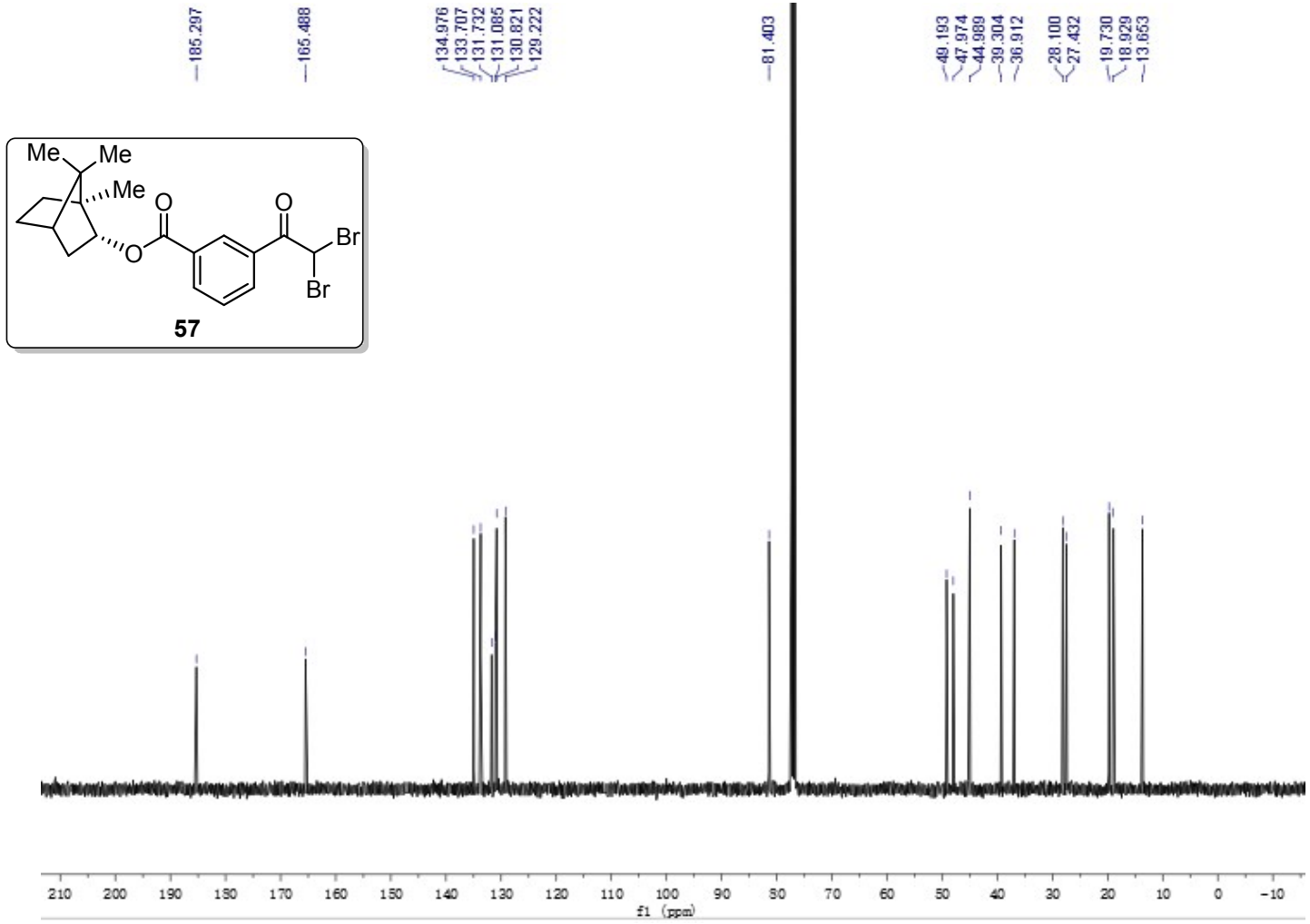
## $^{13}$C NMR of 56


185.334
164.775
135.069
133.617
131.798
131.134
130.709
129.147
75.749
47.217
40.911
39.336
34.247
31.472
26.600
23.667
22.023
20.755
16.578
Me
O
O
O
Br
Br
Me
Me
56
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)

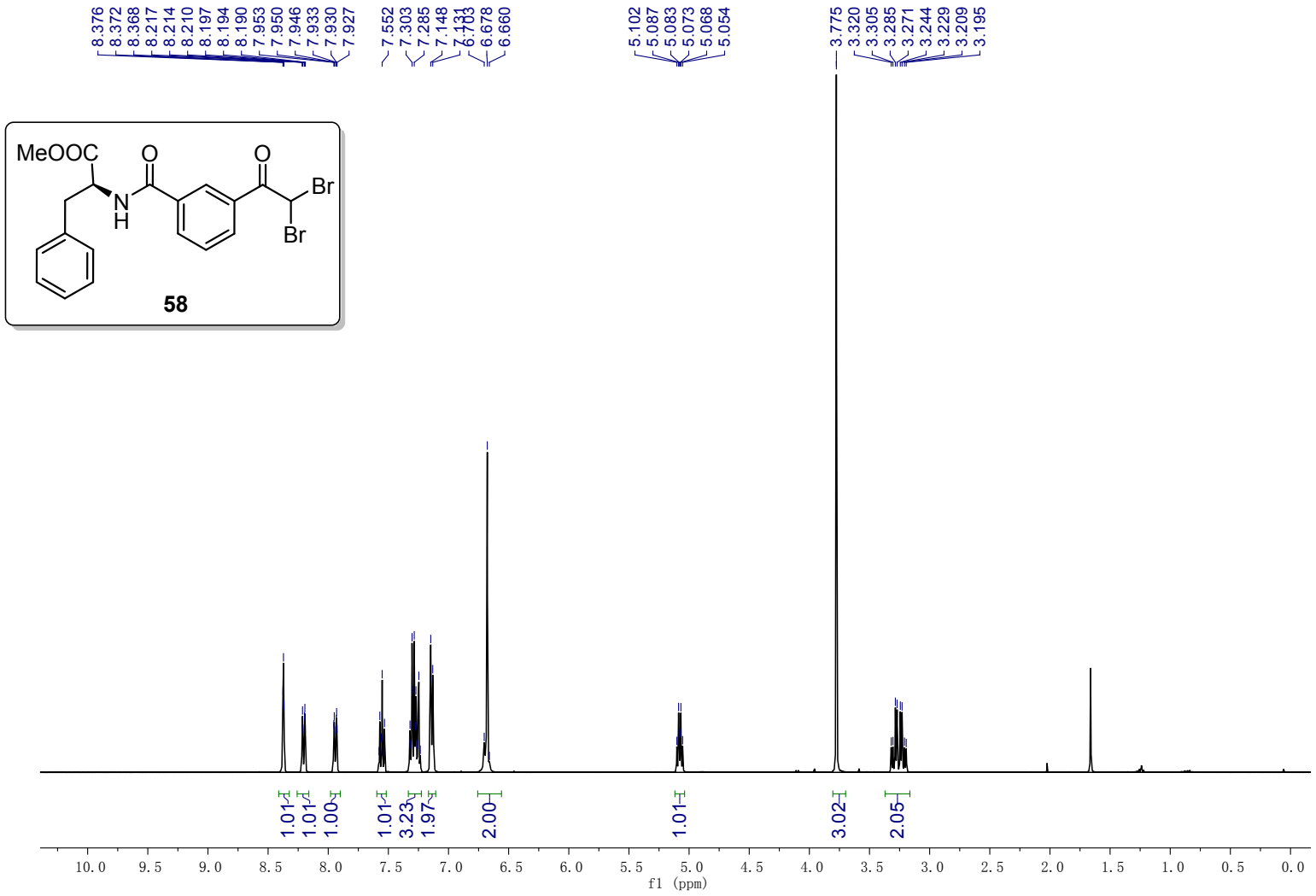
## $^{1}$H NMR of 57



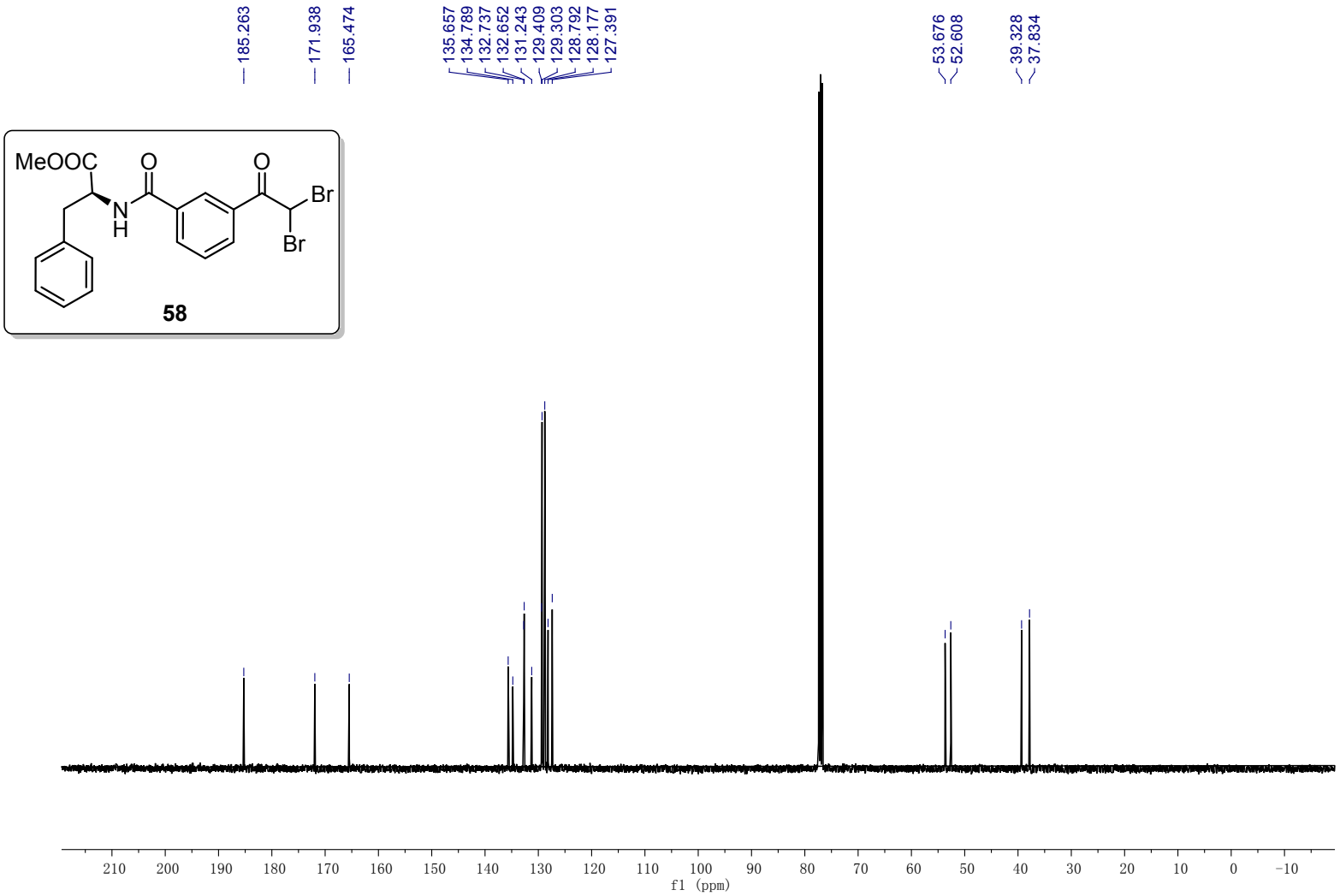
**$^{13}$C NMR of 57**


185.297
165.488
134.976
133.707
131.732
131.085
130.821
129.222
81.403
49.193
47.974
44.989
39.304
36.912
28.100
27.432
19.730
18.929
13.653
Me
Me
Me
O
O
O
Br
Br
57
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)

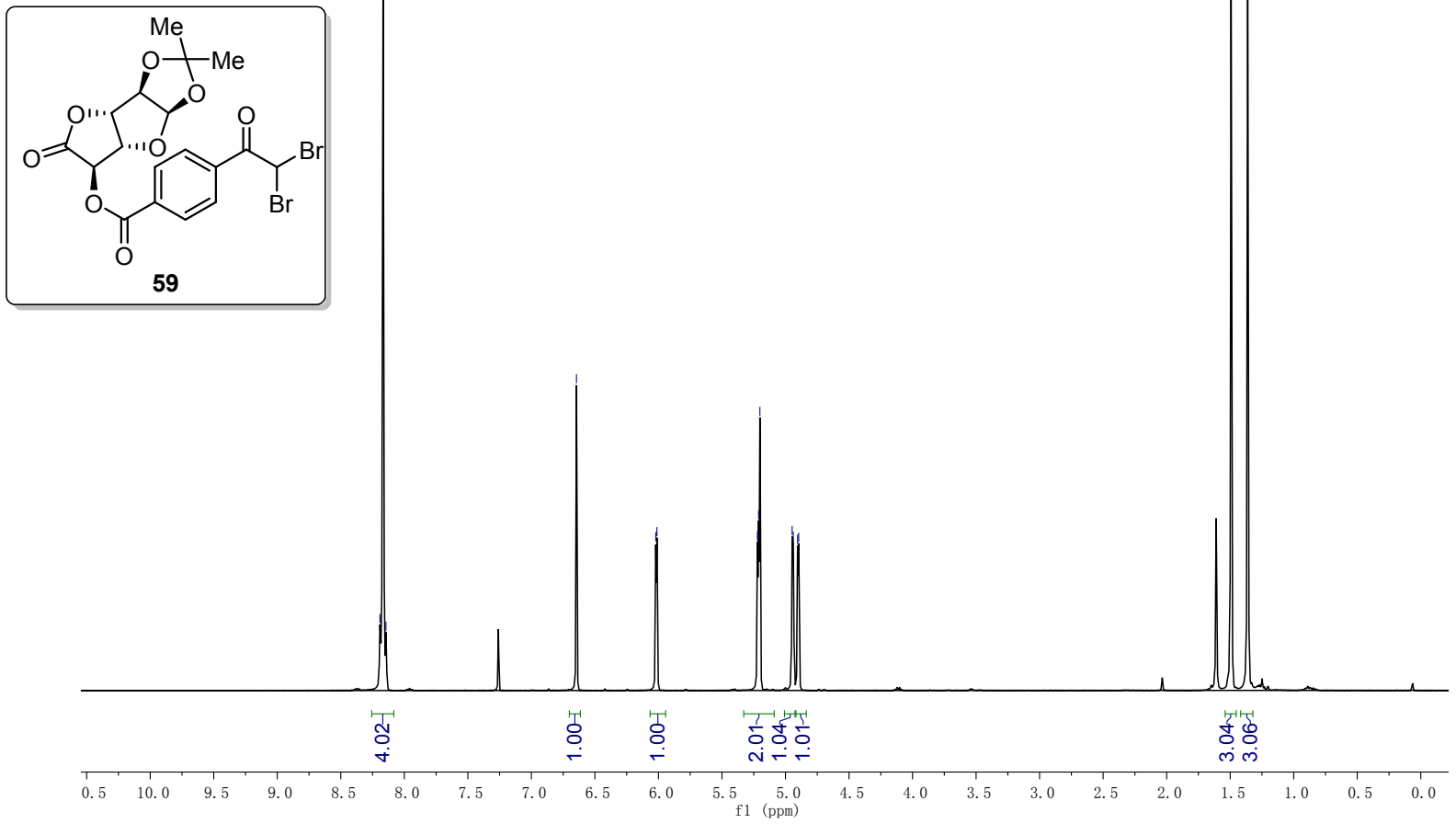
## $^{1}$H NMR of 58


8.376
8.372
8.368
8.217
8.214
8.210
8.197
8.194
8.190
7.953
7.950
7.946
7.933
7.930
7.927
7.552
7.303
7.285
7.148
7.131
7.103
6.678
6.660
5.102
5.087
5.083
5.073
5.068
5.054
3.775
3.320
3.305
3.285
3.271
3.244
3.229
3.209
3.195
MeOOC
O
O
N
H
Br
Br
58
1.01
1.01
1.00
1.01
3.23
1.97
2.00
1.01
3.02
2.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

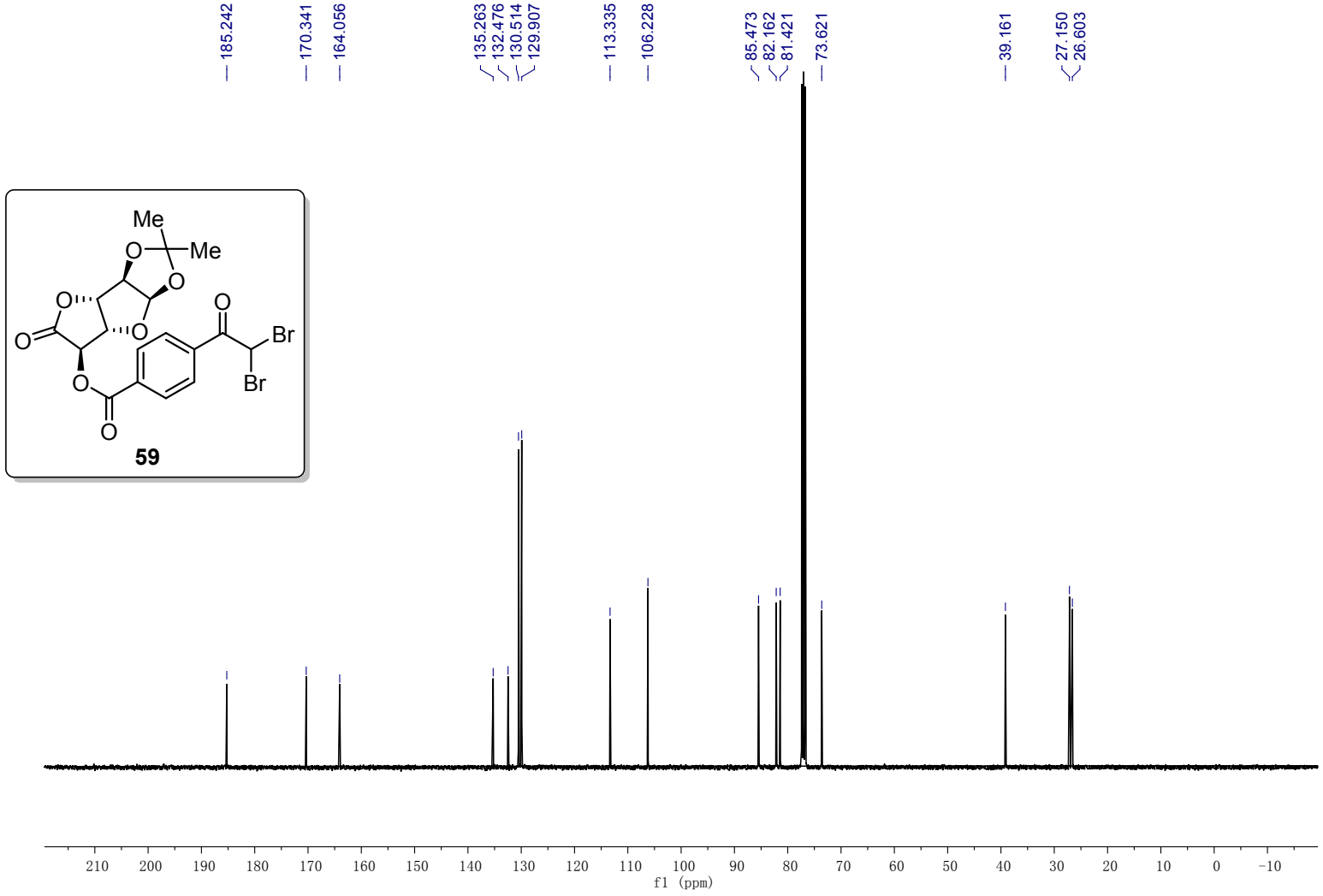
## $^{13}$C NMR of 58


185.263
171.938
165.474
135.657
134.789
132.737
132.652
131.243
129.409
129.303
128.792
128.177
127.391
53.676
52.608
39.328
37.834
MeOOC
O
O
N
H
Br
Br
58
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)

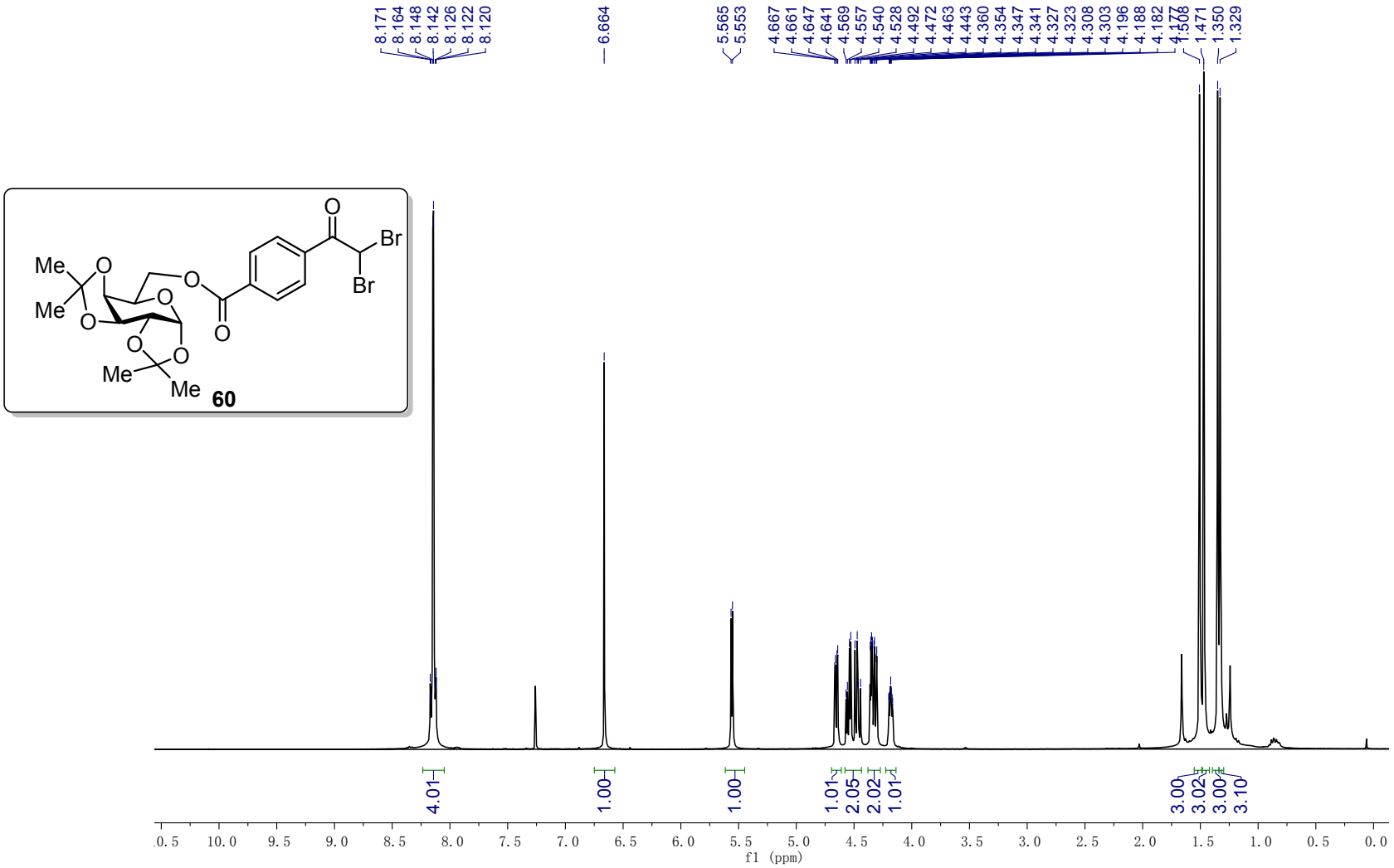
## $^{1}$H NMR of 59


8.192
8.167
8.144
6.645
6.021
6.012
5.221
5.212
5.201
4.948
4.939
4.905
4.896
1.493
1.363
Me
Me
O
O
O
O
O
O
O
Br
Br
O
59
4.02
1.00
1.00
2.01
1.04
1.01
3.04
3.06
f1 (ppm)

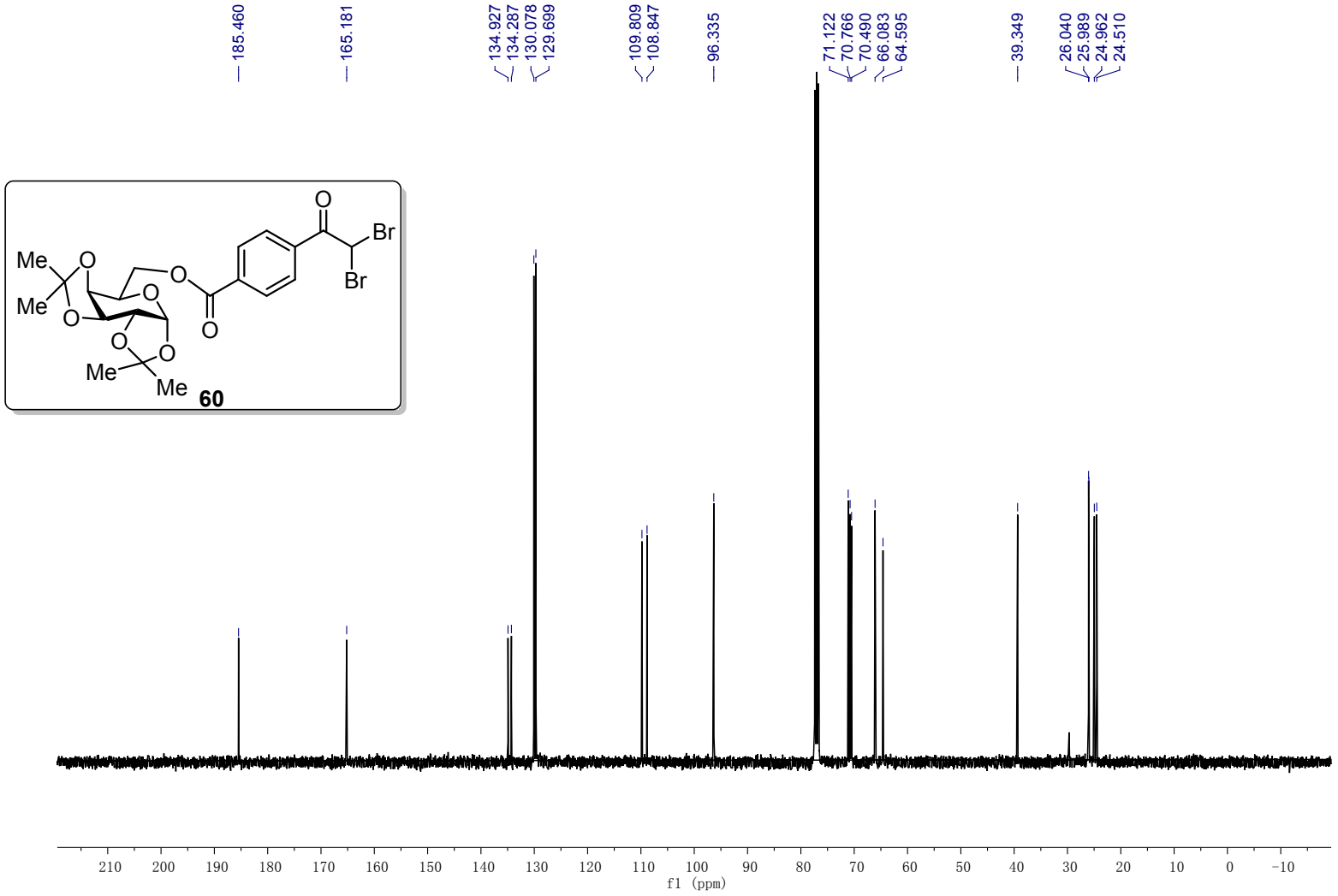
## $^{13}$C NMR of 59


185.242
170.341
164.056
135.263
132.476
130.514
129.907
113.335
106.228
85.473
82.162
81.421
73.621
39.161
27.150
26.603
Me
Me
O
O
O
O
O
O
O
O
Br
Br
59
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)

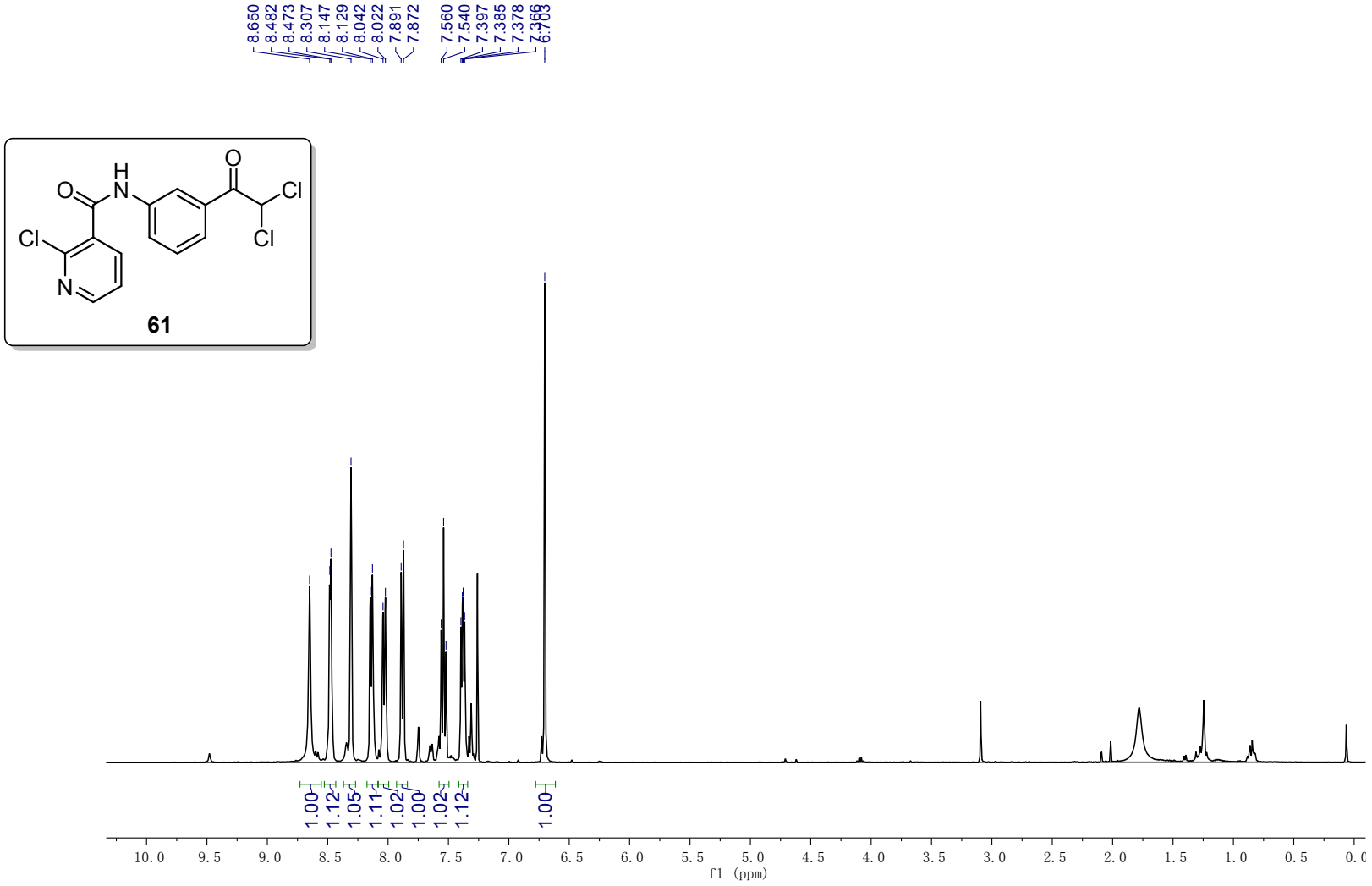
## $^{1}$H NMR of 60


8.171
8.164
8.148
8.142
8.126
8.122
8.120
6.664
5.565
5.553
4.667
4.661
4.647
4.641
4.569
4.557
4.540
4.528
4.492
4.472
4.463
4.443
4.360
4.354
4.347
4.341
4.327
4.323
4.308
4.303
4.196
4.188
4.182
1.508
1.471
1.350
1.329
Me
Me
Me
Me
O
O
O
O
O
O
O
O
Br
Br
60
4.01
1.00
1.00
1.01
2.05
2.02
1.01
3.00
3.02
3.00
3.10
f1 (ppm)

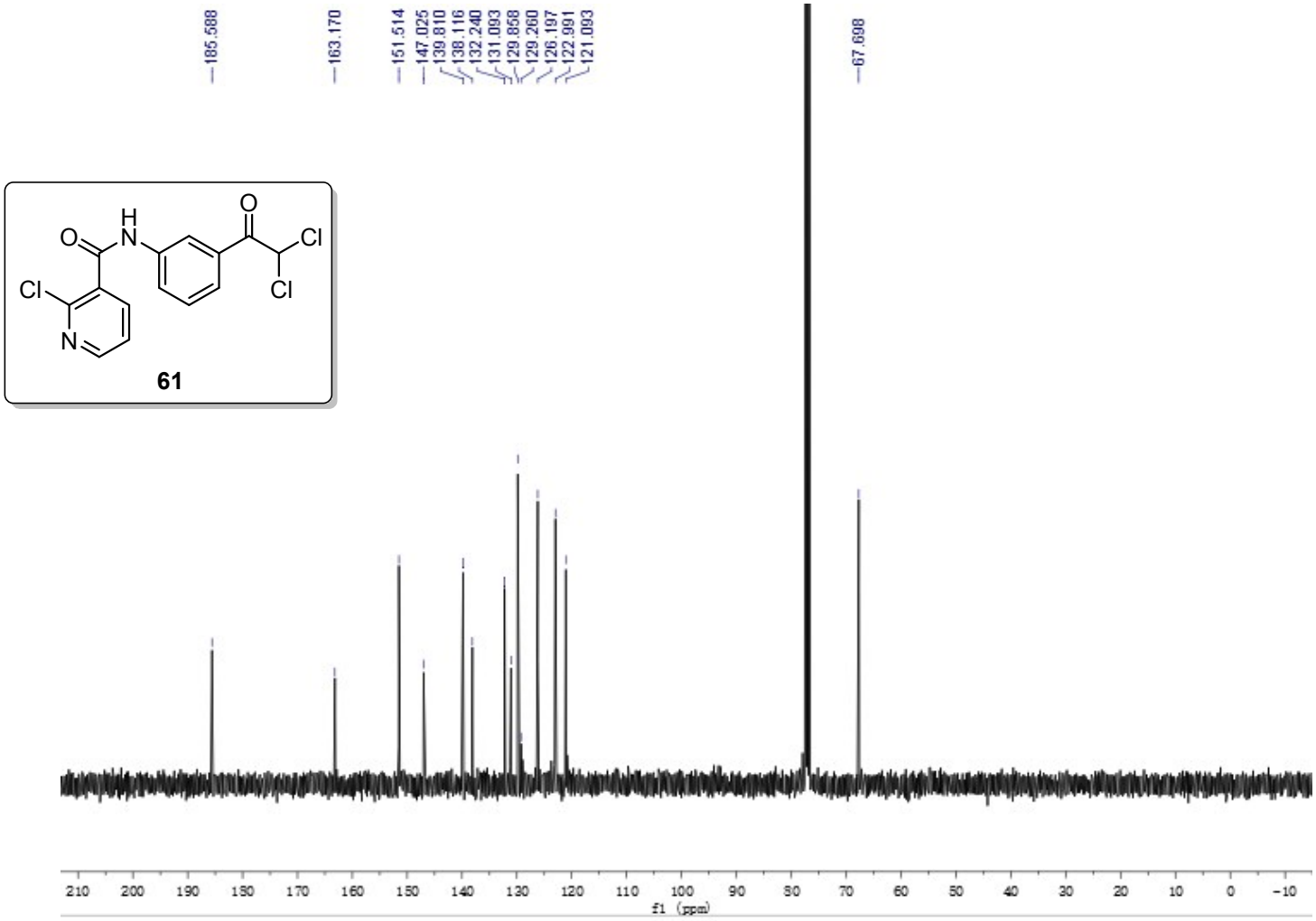
## $^{13}$C NMR of 60


185.460
165.181
134.927
134.287
130.078
129.699
109.809
108.847
96.335
71.122
70.766
70.490
66.083
64.595
39.349
26.040
25.989
24.962
24.510
Me
Me
O
O
O
O
O
O
O
Br
Br
Me
Me
60
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)

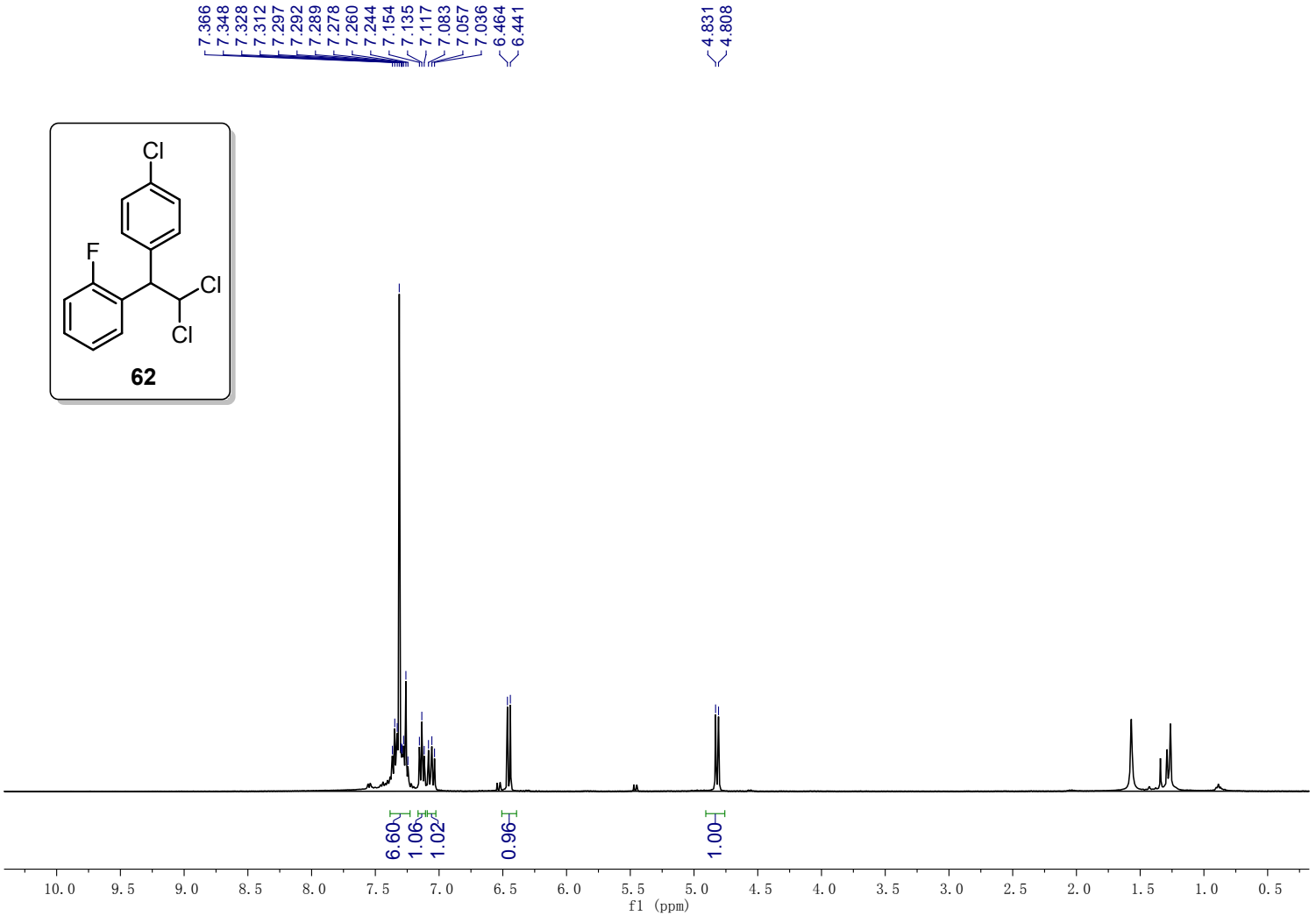
## $^{1}$H NMR of 61


8.650
8.482
8.473
8.307
8.147
8.129
8.042
8.022
7.891
7.872
7.560
7.540
7.397
7.385
7.378
6.703
O
H
N
O
Cl
Cl
Cl
N
61
1.00
1.12
1.05
1.11
1.02
1.00
1.02
1.12
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

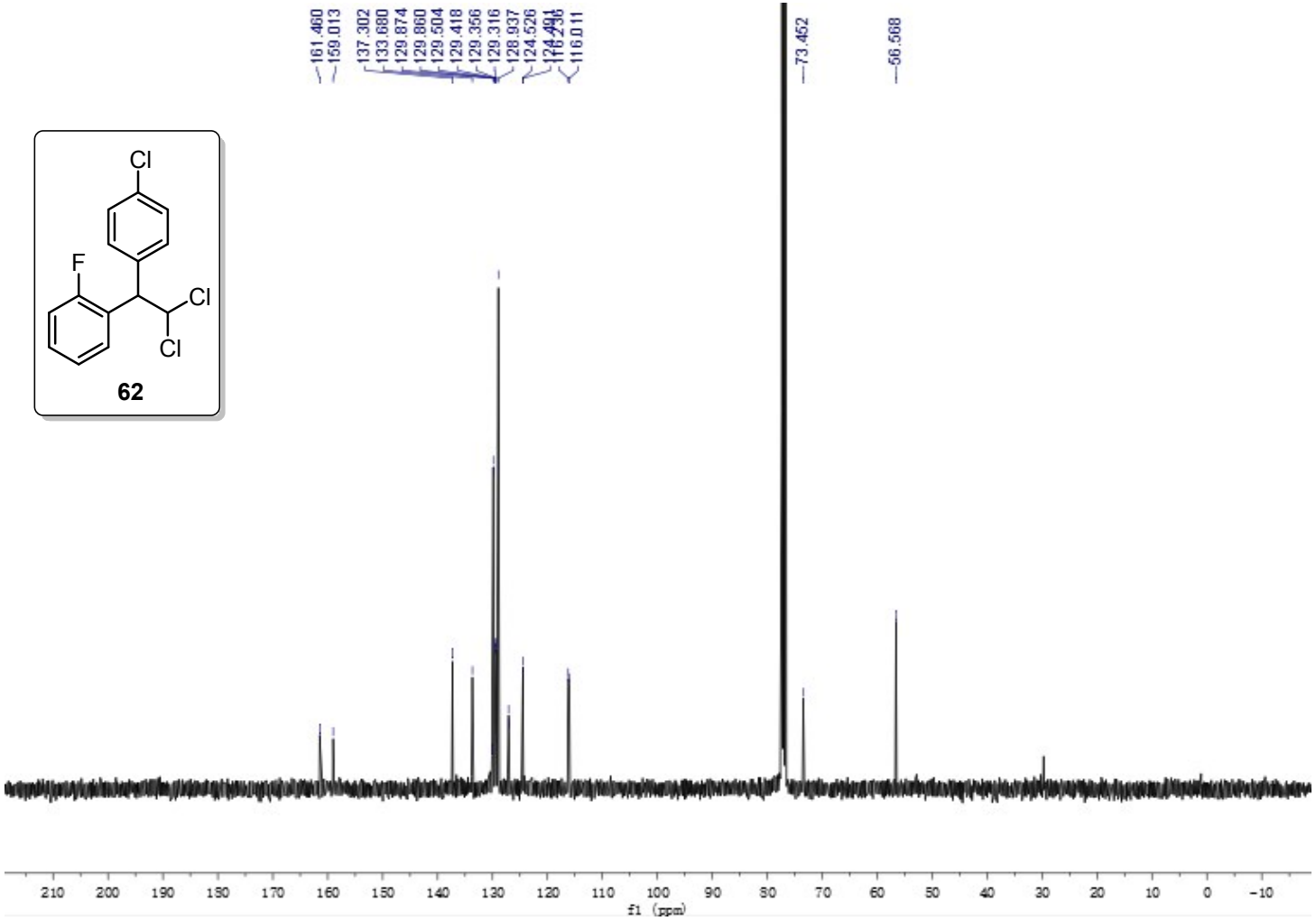
## $^{13}$C NMR of 61


185.588
163.170
151.514
147.025
139.810
138.116
132.240
131.093
129.858
129.260
126.197
122.991
121.093
67.698
O
H
N
O
Cl
Cl
Cl
N
61
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)

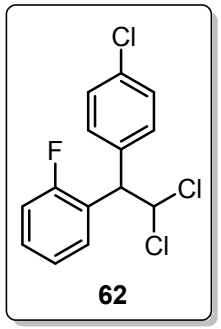
## $^{1}$H NMR of 62


7.366
7.348
7.328
7.312
7.297
7.292
7.289
7.278
7.260
7.244
7.154
7.135
7.117
7.083
7.057
7.036
6.464
6.441
4.831
4.808
Cl
F
Cl
Cl
62
6.60
1.06
1.02
0.96
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

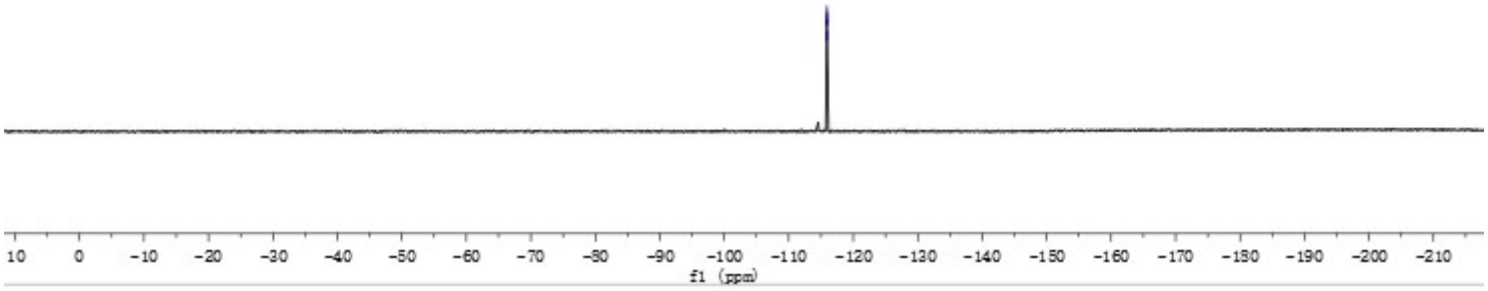
**$^{13}$C NMR of 62**


161.460
159.013
137.302
133.680
129.874
129.860
129.504
129.418
129.356
129.316
128.937
124.526
116.011
73.452
56.568
Cl
F
Cl
Cl
62
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)

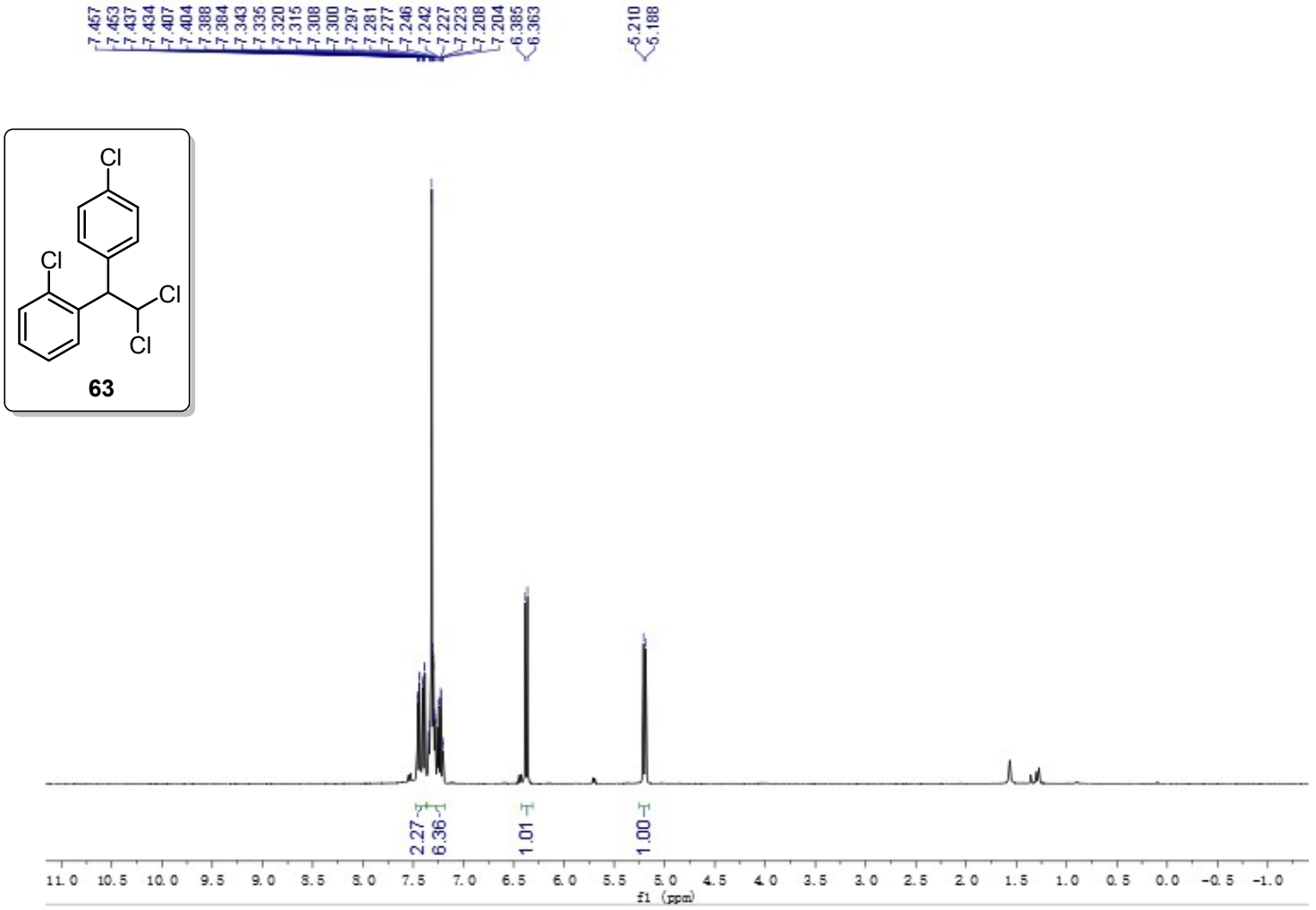
## $^{19}$F NMR of 62

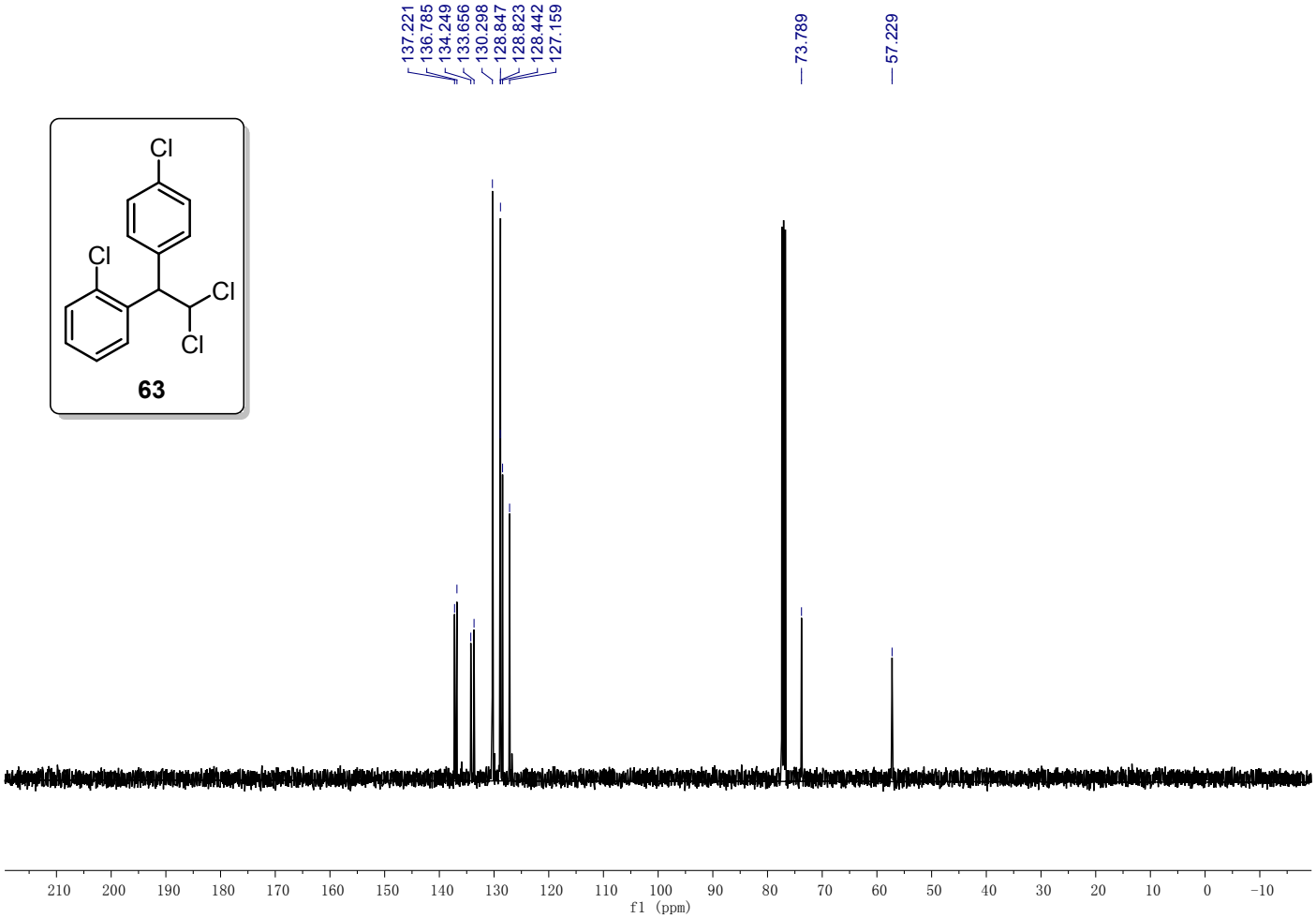

**62**



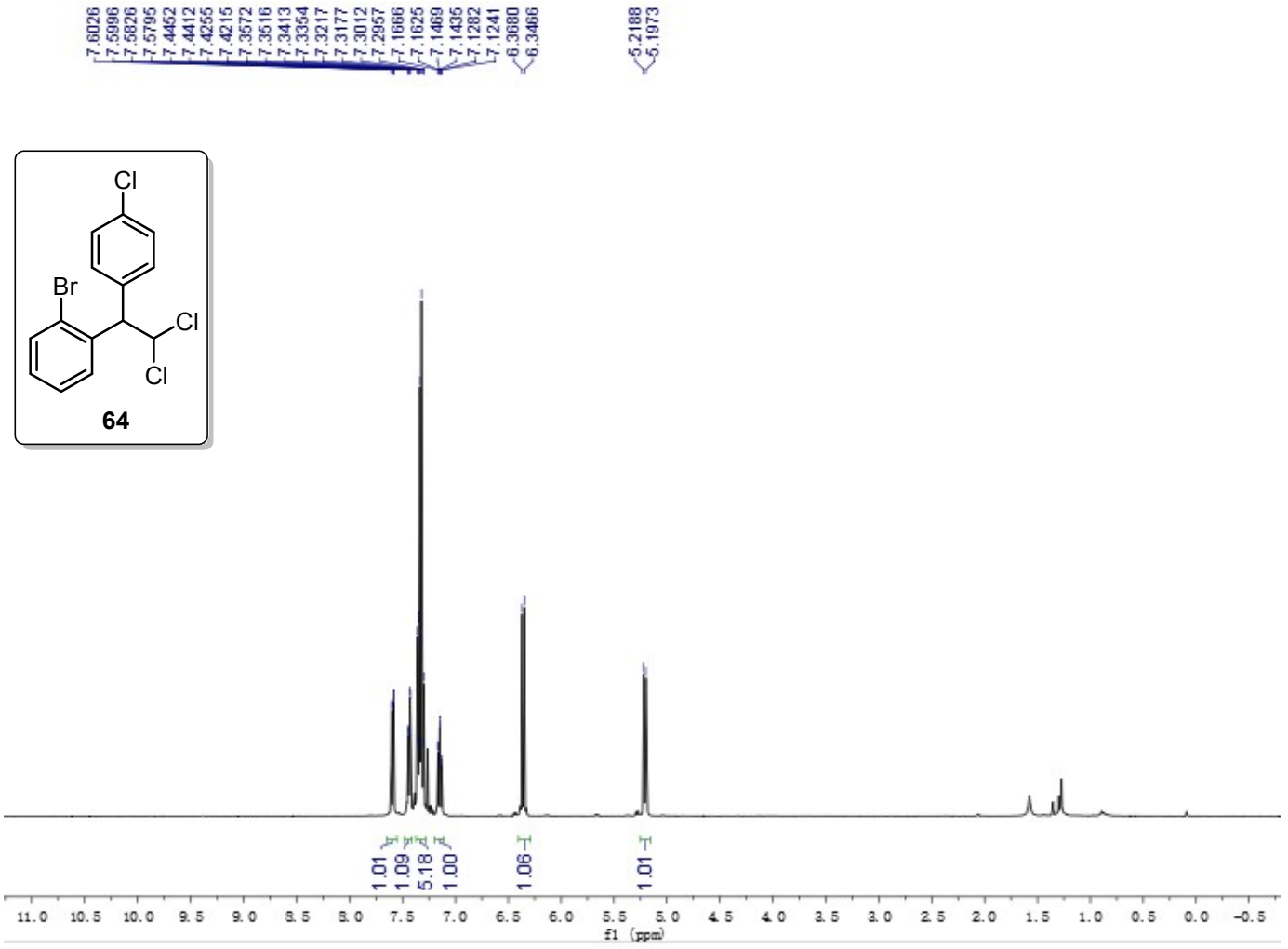
**$^{1}$H NMR of 63**


7.457
7.453
7.437
7.434
7.407
7.404
7.388
7.384
7.343
7.335
7.320
7.315
7.308
7.300
7.297
7.281
7.277
7.246
7.242
7.227
7.223
7.208
7.204
6.385
6.363
5.210
5.188
Cl
Cl
Cl
Cl
63
2.27
6.36
1.01
1.00
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 -1.0
f1 (ppm)

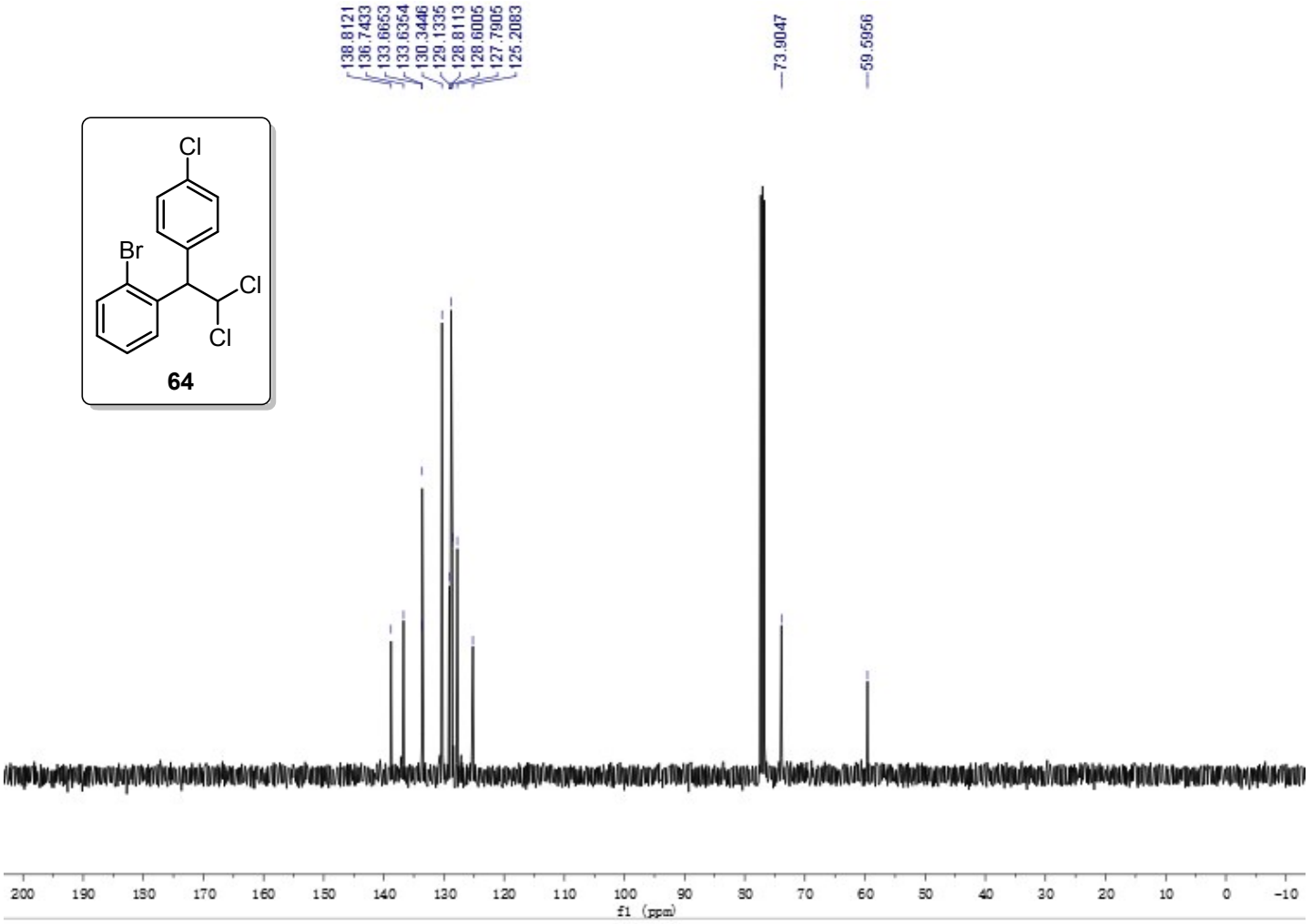
## $^{13}$C NMR of 63


137.221
136.785
134.249
133.656
130.298
128.847
128.823
128.442
127.159
73.789
57.229
Cl
Cl
Cl
Cl
63
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)

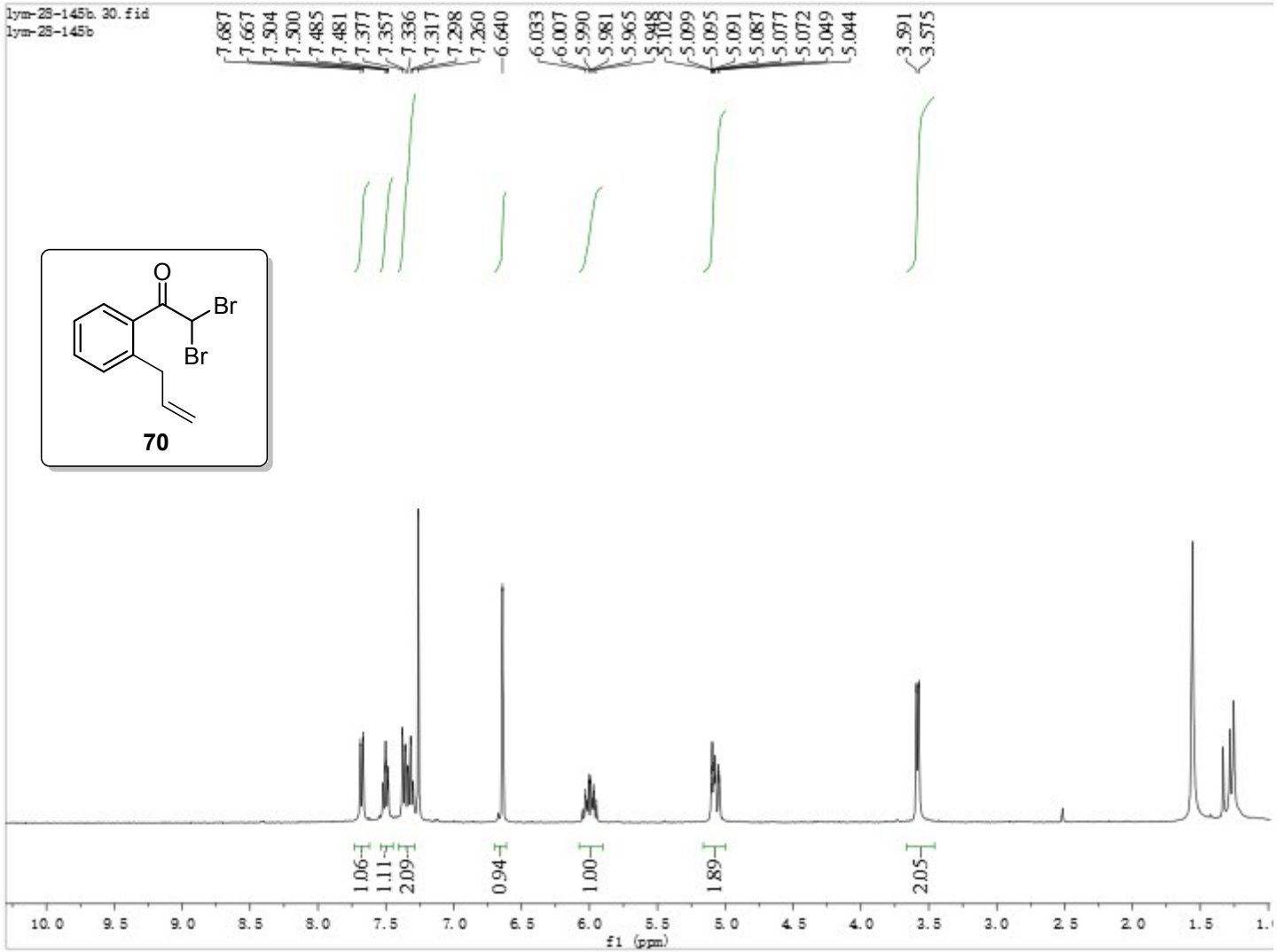
## $^{1}$H NMR of 64


7.6026
7.5996
7.5826
7.5795
7.4452
7.4412
7.4255
7.4215
7.3572
7.3516
7.3413
7.3354
7.3217
7.3177
7.3012
7.2957
7.1666
7.1625
7.1469
7.1435
7.1282
7.1241
6.3680
6.3466
5.2188
5.1973
Cl
Br
Cl
Cl
64
1.01
1.09
5.18
1.00
1.06
1.01
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
f1 (ppm)

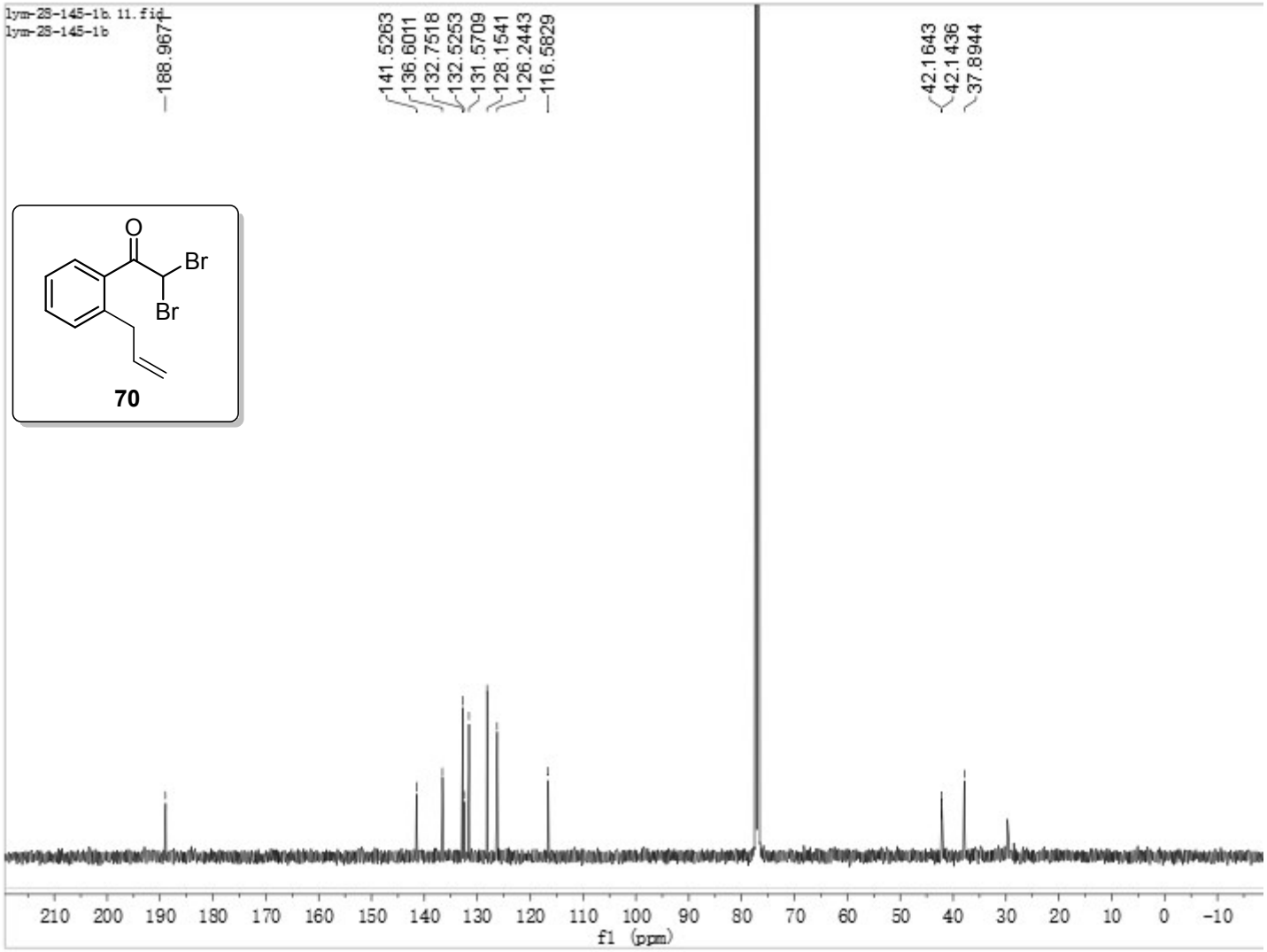
**$^{13}$C NMR of 64**


138.8121
136.7433
133.6653
133.6354
130.3446
129.1335
128.8113
128.6005
127.7905
125.2083
73.9047
59.5956
Cl
Br
Cl
Cl
64
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

**$^{1}$H NMR of 70**


lym-28-145b.30.fid
lym-28-145b
7.687
7.667
7.504
7.500
7.485
7.481
7.377
7.357
7.336
7.317
7.298
7.260
6.640
6.033
6.007
5.990
5.981
5.965
5.948
5.102
5.099
5.095
5.091
5.087
5.077
5.072
5.049
5.044
3.591
3.575
O
Br
Br
70
1.06
1.11
2.09
0.94
1.00
1.89
2.05
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
f1 (ppm)

**$^{13}$C NMR of 70**


lym-28-145-1b.11.fid
lym-28-145-1b
188.9671
141.5263
136.6011
132.7518
132.5253
131.5709
128.1541
126.2443
116.5829
42.1643
42.1436
37.8944
O
Br
Br
70
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)

# VI. References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