

# Visible-Light-Induced Difunctionalization of the C-C Bond of Alkylidenecyclopropanes with Acyl Chlorides

Chuan Ding <sup>†</sup>, Peng-Fei Huang <sup>†</sup>, Biquan Xiong, Ke-Wen Tang <sup>\*</sup> and Yu Liu <sup>\*</sup>

Department of Chemistry and Chemical Engineering, Hunan Institute of Science and Technology, Yueyang 414006, China; pengfeihuang@whu.edu.cn (P.-F.H.)

<sup>\*</sup> Correspondence: tangkewen@sina.com (K.-W.T.); 12015015@hnist.edu.cn (Y.L.)

<sup>†</sup> These authors contributed equally to this work.

## List of Contents

|   |          |
|---|----------|
| 1. 1.General Information                                | S1       |
| 2. Experimental Section                                 | S1-S9    |
| a. General Procedure for the Synthesis of substrates    | S1       |
| b. Typical Experimental Procedure                       | S1-S2    |
| c. Details of Visible-Light Source                      | S2       |
| d. The Light on/off Experiments                         | S2-S3    |
| e. Control Experiments                                  | S3-S15   |
| 3. Reference  | S16      |
| 4. <sup>1</sup> H and <sup>13</sup> C spectra           | S16-S94  |
| 5. The X-ray Single-Crystal Diffraction Analysis of 3ad | S89-S103 |

## 1. General Information

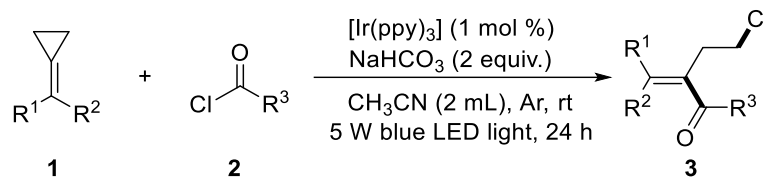
Unless otherwise stated, all commercial reagents were used as received. benzoyl chloride (MERYER, 99%), Aryl ketone (Ark Pharm, 95%), NaH (Innochem, >98%) and Grignard reagent (Innochem, >98%) were used without further treatment. All reagents and solvents were commercially available and used without any further purification unless specified. All solvents were dried and distilled according to standard procedures. Flash column chromatography was performed using silica gel (0.25mm, 300-400 mesh). Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25mm 300-400 mesh silica gel impregnated with a fluorescent indicator (254 nm). All reactions were carried out with magnetic stirring and in dried glassware. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the  $\delta$  scale. <sup>1</sup>H NMR, <sup>19</sup>F NMR and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> on a Bruker DRX-400 spectrometer operating at 400 MHz, 376 MHz and 100 MHz, respectively. All chemical shift values are quoted in ppm and coupling constants quoted in Hz. The solvent peak was used as a reference value, for <sup>1</sup>H NMR: TMS = 0.00 ppm, for <sup>13</sup>C NMR: CDCl<sub>3</sub> = 77.00 ppm. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, td = triplet of doublet, q = quartet, m = multiplet, and br = broad. High-resolution mass spectra (HRMS) were obtained on an Agilent mass spectrometer using ESI-TOF (electrospray ionization-time of flight).

## 2. Experiment Section

### a. General Procedure for the Synthesis of Substrates

All Alkylidenecyclopropanes **1**<sup>[1]</sup> were synthesized according to the known methods.

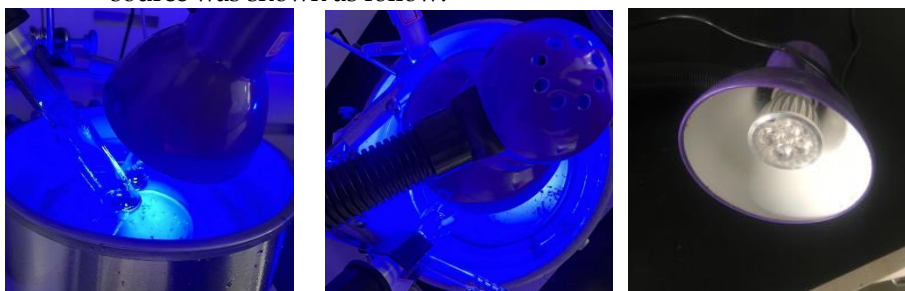
*b. Typical Experimental Procedure*



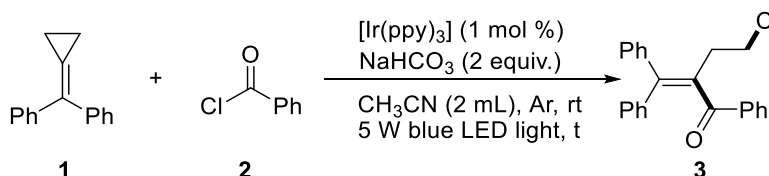
To a Schlenk tube were added **1** (0.2 mmol), **2** (0.4 mmol, 2 equiv),  $\text{CH}_3\text{CN}$  (2 mL),  $\text{Ir}(\text{ppy})_3$  (1 mol%),  $\text{NaHCO}_3$  (2 equiv). Then the mixture was stirred at 25 °C (25 °C referred to the temperature of oil bath in which each reaction Schlenk tube was half immersed ) in Ar atmosphere for 24 h until complete consumption of starting material as monitored by TLC and GC-MS analysis. After the reaction was finished, the reaction mixture was washed with brine. The aqueous phase was re-extracted with EtOAc (3 × 10 mL). The combined organic extracts were dried over  $\text{Na}_2\text{SO}_4$  and concentrated in vacuum. The residue was purified by silica gel flash column chromatography (hexane/ethyl acetate = 100 : 1 to 70 : 1) to afford the desired products **3**.

*c. Details of Visible-Light Source*

The light source bought from SANYI ([https://item.taobao.com/item.htm?spm=a1z09.2.0.0.42672e8dv2Chsz&id=35497290577&\\_u=j35sh1qt9325](https://item.taobao.com/item.htm?spm=a1z09.2.0.0.42672e8dv2Chsz&id=35497290577&_u=j35sh1qt9325)), 5 W blue LED light bulb (E27). The wavelength was about 400-440 nm and the wavelength of peak intensity was about 415.5 nm. The pictures of the visible-light source was shown as follow:

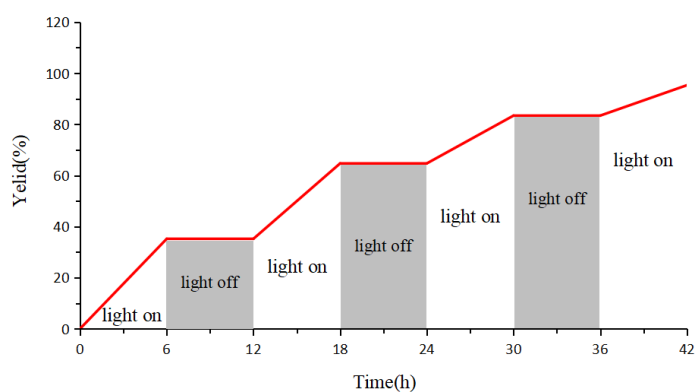


*d. The Light on/off Experiments*



| Time/h  | 0 | 6 (on) | 12 (off) | 18 (on) | 24 (off) | 30 (on) | 36 (off) | 42 (on) |
|---------|---|--------|----------|---------|----------|---------|----------|---------|
| Yield/% | 0 | 35.2   | 35.2     | 64.7    | 64.7     | 83.4    | 83.4     | 94.3    |

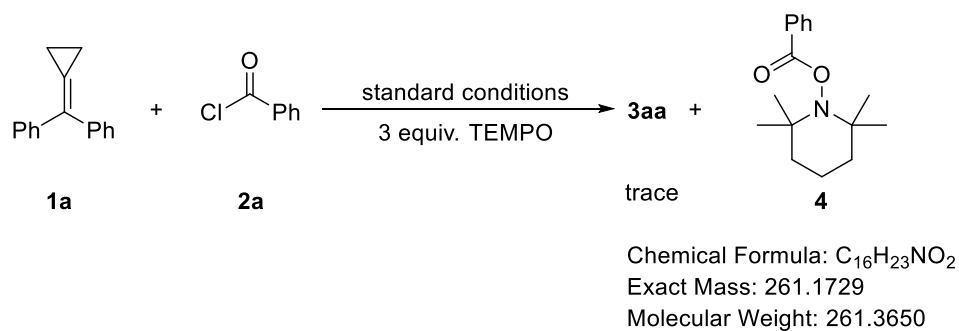
The above depicted reaction was performed according to the general protocol established. The reaction was irradiated with 5 W blue LEDs for 8 hour and then stirred in the dark for 8 hour. This procedure was repeated for 42 hours, and the yield of the product was determined by  $^1\text{H}$  NMR with dibromomethane as an internal standard at each point the light was turned off or on. The results are shown in the graph above. This result shows that constant light irradiation is needed to progress the reaction.



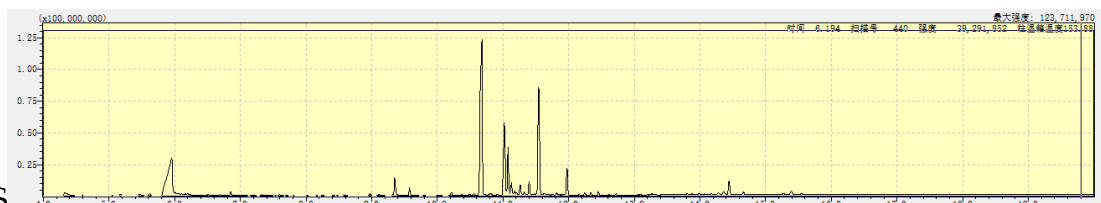
### The Light on/off Experiments

#### e. Control Experiments

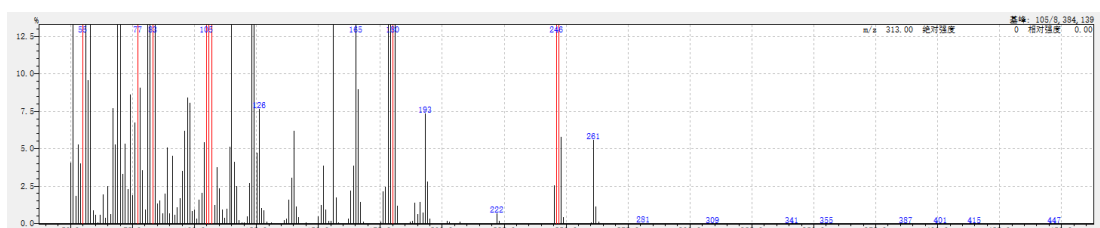
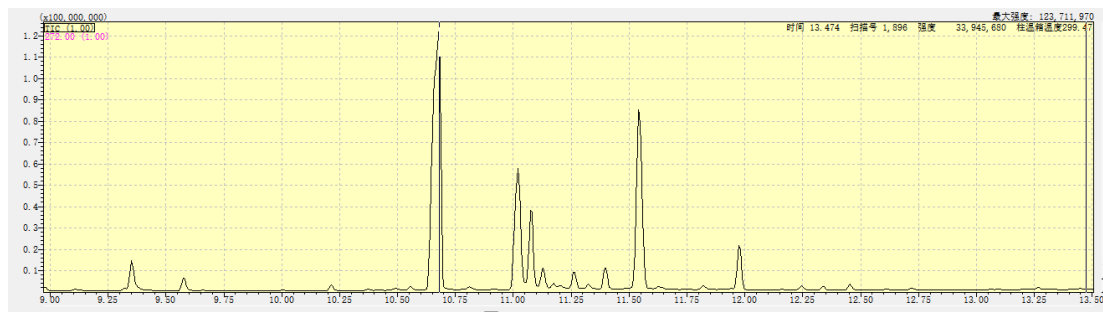
##### 2.3.1. GC-MS Analysis of Raw Reaction Mixture by Using TEMPO as Radical Inhibitor



Spectra of GC-MS



MS Spectra of the peak at 10.67 min



---

[MS Spectrum]

# of Peaks 401

Raw Spectrum 10.680 (scan : 1337)

Background No Background Spectrum

Base Peak m/z 104.95 (Inten : 8,384,139)

Event# 1

| m/z | Absolute Intensity | Relative Intensity |
|-----|--------------------|--------------------|
|-----|--------------------|--------------------|

|       |        |      |
|-------|--------|------|
| 50.05 | 344707 | 4.11 |
|-------|--------|------|

|       |         |       |
|-------|---------|-------|
| 51.00 | 1700884 | 20.29 |
|-------|---------|-------|

|       |        |      |
|-------|--------|------|
| 52.05 | 155164 | 1.85 |
|-------|--------|------|

|       |        |      |
|-------|--------|------|
| 53.00 | 444890 | 5.31 |
|-------|--------|------|

|       |        |      |
|-------|--------|------|
| 54.05 | 337042 | 4.02 |
|-------|--------|------|

|       |         |       |
|-------|---------|-------|
| 55.05 | 8330822 | 99.36 |
|-------|---------|-------|

|       |         |       |
|-------|---------|-------|
| 56.05 | 4922888 | 58.72 |
|-------|---------|-------|

|       |        |      |
|-------|--------|------|
| 57.10 | 805559 | 9.61 |
|-------|--------|------|

|       |         |       |
|-------|---------|-------|
| 58.05 | 1669788 | 19.92 |
|-------|---------|-------|

|       |           |  |
|-------|-----------|--|
| 59.05 | 745870.89 |  |
|-------|-----------|--|

|       |           |  |
|-------|-----------|--|
| 60.05 | 509110.61 |  |
|-------|-----------|--|

|       |      |      |
|-------|------|------|
| 61.05 | 9517 | 0.11 |
|-------|------|------|

|       |           |  |
|-------|-----------|--|
| 62.05 | 510340.61 |  |
|-------|-----------|--|

|       |        |      |
|-------|--------|------|
| 63.00 | 166090 | 1.98 |
|-------|--------|------|

|       |           |  |
|-------|-----------|--|
| 64.05 | 346600.41 |  |
|-------|-----------|--|

|       |        |      |
|-------|--------|------|
| 65.00 | 212716 | 2.54 |
|-------|--------|------|

|       |           |  |
|-------|-----------|--|
| 66.05 | 544450.65 |  |
|-------|-----------|--|

|       |        |      |
|-------|--------|------|
| 67.05 | 646584 | 7.71 |
|-------|--------|------|

|       |        |      |
|-------|--------|------|
| 68.15 | 446113 | 5.32 |
|-------|--------|------|

|       |         |       |
|-------|---------|-------|
| 69.05 | 4748403 | 56.64 |
|-------|---------|-------|

|       |         |       |
|-------|---------|-------|
| 70.05 | 1287673 | 15.36 |
|-------|---------|-------|

|       |        |      |
|-------|--------|------|
| 71.05 | 280022 | 3.34 |
|-------|--------|------|

|       |        |      |
|-------|--------|------|
| 72.05 | 450970 | 5.38 |
|-------|--------|------|

|       |        |      |
|-------|--------|------|
| 73.05 | 196275 | 2.34 |
|-------|--------|------|

|       |        |      |
|-------|--------|------|
| 74.05 | 724489 | 8.64 |
|-------|--------|------|

|       |        |      |
|-------|--------|------|
| 75.05 | 159915 | 1.91 |
|-------|--------|------|

|       |        |      |
|-------|--------|------|
| 76.05 | 569253 | 6.79 |
|-------|--------|------|

|       |         |       |
|-------|---------|-------|
| 77.00 | 7932513 | 94.61 |
|-------|---------|-------|

|       |        |      |
|-------|--------|------|
| 78.05 | 760769 | 9.07 |
|-------|--------|------|

|       |        |      |
|-------|--------|------|
| 79.05 | 298892 | 3.56 |
|-------|--------|------|

|       |           |  |
|-------|-----------|--|
| 80.15 | 816120.97 |  |
|-------|-----------|--|

|       |         |       |
|-------|---------|-------|
| 81.10 | 1546094 | 18.44 |
|-------|---------|-------|

|       |         |       |
|-------|---------|-------|
| 82.15 | 1492896 | 17.81 |
|-------|---------|-------|

|       |         |       |
|-------|---------|-------|
| 83.10 | 8151922 | 97.23 |
|-------|---------|-------|

|       |         |       |
|-------|---------|-------|
| 84.10 | 1424458 | 16.99 |
|-------|---------|-------|

|       |        |      |
|-------|--------|------|
| 85.10 | 113031 | 1.35 |
|-------|--------|------|

|       |        |      |
|-------|--------|------|
| 86.05 | 130645 | 1.56 |
|-------|--------|------|

|       |           |  |
|-------|-----------|--|
| 87.05 | 604340.72 |  |
|-------|-----------|--|

|       |        |      |
|-------|--------|------|
| 88.10 | 168012 | 2.00 |
|-------|--------|------|

|       |        |      |
|-------|--------|------|
| 89.05 | 428106 | 5.11 |
|-------|--------|------|

|       |           |  |
|-------|-----------|--|
| 90.05 | 580600.69 |  |
|-------|-----------|--|

|       |        |      |
|-------|--------|------|
| 91.05 | 379706 | 4.53 |
|-------|--------|------|

|       |           |  |
|-------|-----------|--|
| 92.05 | 509130.61 |  |
|-------|-----------|--|

---

|        |           |        |
|--------|-----------|--------|
| 93.10  | 943031.12 |        |
| 94.15  | 143985    | 1.72   |
| 95.05  | 298614    | 3.56   |
| 96.10  | 520913    | 6.21   |
| 97.10  | 708153    | 8.45   |
| 98.10  | 676583    | 8.07   |
| 99.10  | 720440.86 |        |
| 100.10 | 786120.94 |        |
| 100.95 | 288040.34 |        |
| 101.95 | 135362    | 1.61   |
| 102.95 | 174182    | 2.08   |
| 103.95 | 457965    | 5.46   |
| 104.95 | 8384139   | 100.00 |
| 105.90 | 8382558   | 99.98  |
| 106.85 | 1678313   | 20.02  |
| 108.10 | 105254    | 1.26   |
| 109.15 | 319623    | 3.81   |
| 110.10 | 200151    | 2.39   |
| 111.10 | 820650.98 |        |
| 112.15 | 333130.40 |        |
| 113.10 | 828760.99 |        |
| 114.15 | 432854    | 5.16   |
| 115.05 | 1201272   | 14.33  |
| 116.10 | 348860    | 4.16   |
| 117.10 | 210812    | 2.51   |
| 118.10 | 219240.26 |        |
| 119.15 | 6405      | 0.08   |
| 120.15 | 9216      | 0.11   |
| 121.25 | 436510.52 |        |
| 122.15 | 228260    | 2.72   |
| 123.15 | 1858108   | 22.16  |
| 124.15 | 2227434   | 26.57  |
| 125.15 | 397615    | 4.74   |
| 126.15 | 643009    | 7.67   |
| 127.15 | 906991.08 |        |
| 128.10 | 751580.90 |        |
| 129.10 | 141750.17 |        |
| 130.15 | 3629      | 0.04   |
| 131.05 | 7632      | 0.09   |
| 132.15 | 2548      | 0.03   |
| 133.15 | 2649      | 0.03   |
| 134.15 | 5611      | 0.07   |
| 135.15 | 5455      | 0.07   |
| 136.15 | 215860.26 |        |
| 137.15 | 285380.34 |        |
| 138.15 | 136740    | 1.63   |
| 139.15 | 260231    | 3.10   |
| 140.15 | 521545    | 6.22   |
| 141.15 | 988381.18 |        |
| 142.15 | 388140.46 |        |
| 143.15 | 5581      | 0.07   |
| 144.10 | 3727      | 0.04   |

---

|        |           |       |
|--------|-----------|-------|
| 145.10 | 6545      | 0.08  |
| 146.10 | 2807      | 0.03  |
| 147.10 | 5559      | 0.07  |
| 148.10 | 2218      | 0.03  |
| 149.15 | 5799      | 0.07  |
| 150.05 | 421050.50 |       |
| 151.10 | 104762    | 1.25  |
| 152.05 | 328334    | 3.92  |
| 153.05 | 822600.98 |       |
| 154.10 | 160010.19 |       |
| 155.15 | 149510.18 |       |
| 156.15 | 1504325   | 17.94 |
| 157.10 | 149846    | 1.79  |
| 158.15 | 105930.13 |       |
| 159.10 | 6321      | 0.08  |
| 160.10 | 2814      | 0.03  |
| 161.05 | 5941      | 0.07  |
| 162.15 | 314560.38 |       |
| 163.05 | 186421    | 2.22  |
| 164.15 | 325991    | 3.89  |
| 165.10 | 4496215   | 53.63 |
| 166.05 | 754929    | 9.00  |
| 167.05 | 121311    | 1.45  |
| 168.10 | 138550.17 |       |
| 169.10 | 2004      | 0.02  |
| 170.10 | 3946      | 0.05  |
| 171.05 | 3698      | 0.04  |
| 172.10 | 2572      | 0.03  |
| 173.15 | 2202      | 0.03  |
| 174.10 | 5393      | 0.06  |
| 175.15 | 133770.16 |       |
| 176.05 | 183221    | 2.19  |
| 177.15 | 206012    | 2.46  |
| 178.10 | 2033018   | 24.25 |
| 179.10 | 3292705   | 39.27 |
| 180.10 | 6953276   | 82.93 |
| 181.05 | 1333205   | 15.90 |
| 182.00 | 101238    | 1.21  |
| 182.95 | 5574      | 0.07  |
| 183.95 | 799       | 0.01  |
| 185.05 | 1122      | 0.01  |
| 186.05 | 1319      | 0.02  |
| 187.05 | 121860.15 |       |
| 188.05 | 182800.22 |       |
| 189.05 | 117086    | 1.40  |
| 190.05 | 566750.68 |       |
| 191.05 | 121923    | 1.45  |
| 192.15 | 647930.77 |       |
| 193.10 | 618812    | 7.38  |
| 194.05 | 239015    | 2.85  |
| 195.05 | 308920.37 |       |
| 196.10 | 2303      | 0.03  |

---

|        |           |       |
|--------|-----------|-------|
| 197.05 | 979       | 0.01  |
| 198.10 | 657       | 0.01  |
| 199.05 | 643       | 0.01  |
| 200.05 | 3198      | 0.04  |
| 201.15 | 3563      | 0.04  |
| 202.05 | 162820.19 |       |
| 203.05 | 119050.14 |       |
| 204.05 | 5157      | 0.06  |
| 205.05 | 6270      | 0.07  |
| 206.05 | 3535      | 0.04  |
| 207.05 | 115870.14 |       |
| 208.05 | 2661      | 0.03  |
| 209.00 | 1428      | 0.02  |
| 210.00 | 1436      | 0.02  |
| 211.05 | 598       | 0.01  |
| 212.05 | 4409      | 0.05  |
| 213.20 | 1199      | 0.01  |
| 214.10 | 602       | 0.01  |
| 215.05 | 615       | 0.01  |
| 216.05 | 570       | 0.01  |
| 217.05 | 952       | 0.01  |
| 218.05 | 5457      | 0.07  |
| 219.00 | 4065      | 0.05  |
| 220.05 | 2597      | 0.03  |
| 221.15 | 4814      | 0.06  |
| 222.10 | 592020.71 |       |
| 223.05 | 159370.19 |       |
| 224.20 | 2258      | 0.03  |
| 225.05 | 474       | 0.01  |
| 226.10 | 391       | 0.00  |
| 227.15 | 547       | 0.01  |
| 228.15 | 2372      | 0.03  |
| 229.10 | 1033      | 0.01  |
| 230.05 | 6122      | 0.07  |
| 231.10 | 1111      | 0.01  |
| 232.10 | 785       | 0.01  |
| 233.05 | 306       | 0.00  |
| 234.10 | 154       | 0.00  |
| 235.05 | 424       | 0.01  |
| 236.05 | 291       | 0.00  |
| 237.10 | 390       | 0.00  |
| 238.10 | 218       | 0.00  |
| 239.05 | 846       | 0.01  |
| 240.15 | 325       | 0.00  |
| 241.15 | 355       | 0.00  |
| 242.10 | 614       | 0.01  |
| 243.15 | 836       | 0.01  |
| 244.15 | 3106      | 0.04  |
| 245.15 | 216818    | 2.59  |
| 246.10 | 8336740   | 99.43 |
| 247.05 | 6595950   | 78.67 |
| 248.10 | 486842    | 5.81  |

---

|        |           |      |
|--------|-----------|------|
| 249.05 | 376730.45 |      |
| 250.05 | 2929      | 0.03 |
| 251.00 | 694       | 0.01 |
| 252.25 | 341       | 0.00 |
| 253.25 | 685       | 0.01 |
| 254.25 | 373       | 0.00 |
| 255.05 | 279       | 0.00 |
| 256.00 | 1198      | 0.01 |
| 257.10 | 455       | 0.01 |
| 258.10 | 172       | 0.00 |
| 259.10 | 177       | 0.00 |
| 260.25 | 8398      | 0.10 |
| 261.15 | 469205    | 5.60 |
| 262.15 | 973651.16 |      |
| 263.15 | 118490.14 |      |
| 264.25 | 1165      | 0.01 |
| 265.25 | 833       | 0.01 |
| 266.15 | 232       | 0.00 |
| 267.10 | 1452      | 0.02 |
| 268.05 | 425       | 0.01 |
| 269.00 | 495       | 0.01 |
| 270.00 | 273       | 0.00 |
| 271.00 | 130       | 0.00 |
| 272.00 | 154       | 0.00 |
| 273.00 | 95        | 0.00 |
| 274.00 | 188       | 0.00 |
| 275.00 | 158       | 0.00 |
| 276.00 | 186       | 0.00 |
| 277.00 | 177       | 0.00 |
| 278.00 | 252       | 0.00 |
| 278.95 | 292       | 0.00 |
| 280.00 | 134       | 0.00 |
| 281.05 | 3661      | 0.04 |
| 282.10 | 886       | 0.01 |
| 283.10 | 1426      | 0.02 |
| 284.10 | 722       | 0.01 |
| 285.10 | 334       | 0.00 |
| 286.10 | 170       | 0.00 |
| 287.10 | 46        | 0.00 |
| 288.10 | 36        | 0.00 |
| 289.10 | 198       | 0.00 |
| 290.10 | 218       | 0.00 |
| 291.10 | 118       | 0.00 |
| 292.00 | 326       | 0.00 |
| 293.00 | 241       | 0.00 |
| 294.00 | 78        | 0.00 |
| 295.10 | 353       | 0.00 |
| 296.10 | 185       | 0.00 |
| 297.10 | 185       | 0.00 |
| 298.10 | 118       | 0.00 |
| 299.10 | 44        | 0.00 |
| 300.10 | 81        | 0.00 |



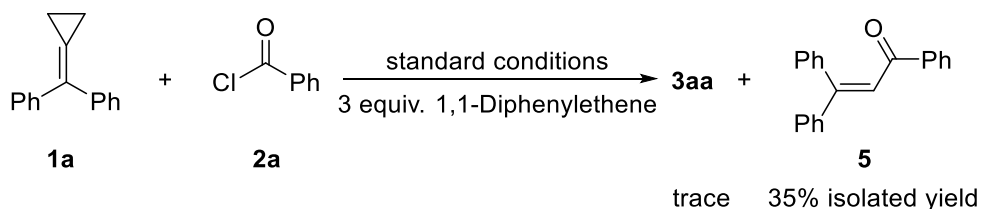
---

|        |      |      |
|--------|------|------|
| 301.10 | 31   | 0.00 |
| 302.10 | 110  | 0.00 |
| 303.10 | 68   | 0.00 |
| 304.10 | 78   | 0.00 |
| 305.10 | 71   | 0.00 |
| 306.10 | 100  | 0.00 |
| 307.10 | 183  | 0.00 |
| 308.10 | 71   | 0.00 |
| 309.10 | 260  | 0.00 |
| 310.10 | 226  | 0.00 |
| 311.10 | 156  | 0.00 |
| 312.10 | 218  | 0.00 |
| 313.10 | 167  | 0.00 |
| 314.10 | 146  | 0.00 |
| 315.10 | 65   | 0.00 |
| 316.10 | 65   | 0.00 |
| 317.10 | 148  | 0.00 |
| 318.10 | 129  | 0.00 |
| 319.10 | 52   | 0.00 |
| 320.10 | 100  | 0.00 |
| 321.10 | 90   | 0.00 |
| 322.10 | 73   | 0.00 |
| 323.10 | 177  | 0.00 |
| 324.10 | 47   | 0.00 |
| 325.10 | 246  | 0.00 |
| 326.05 | 351  | 0.00 |
| 327.00 | 1070 | 0.01 |
| 328.00 | 257  | 0.00 |
| 328.90 | 350  | 0.00 |
| 329.90 | 81   | 0.00 |
| 330.90 | 63   | 0.00 |
| 331.90 | 49   | 0.00 |
| 332.90 | 41   | 0.00 |
| 333.90 | 49   | 0.00 |
| 334.90 | 92   | 0.00 |
| 335.90 | 57   | 0.00 |
| 336.90 | 138  | 0.00 |
| 337.90 | 74   | 0.00 |
| 338.90 | 57   | 0.00 |
| 340.00 | 100  | 0.00 |
| 341.05 | 1579 | 0.02 |
| 342.10 | 1004 | 0.01 |
| 343.10 | 377  | 0.00 |
| 344.10 | 260  | 0.00 |
| 345.10 | 114  | 0.00 |
| 346.10 | 36   | 0.00 |
| 347.10 | 76   | 0.00 |
| 348.10 | 21   | 0.00 |
| 349.10 | 31   | 0.00 |
| 350.10 | 130  | 0.00 |
| 351.10 | 66   | 0.00 |
| 352.10 | 50   | 0.00 |

---

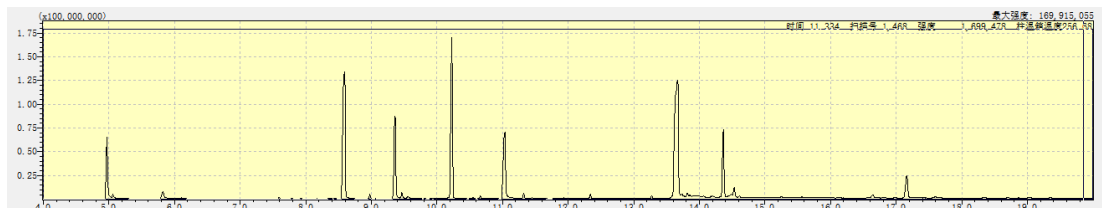
|        |      |      |
|--------|------|------|
| 353.10 | 49   | 0.00 |
| 354.20 | 119  | 0.00 |
| 355.15 | 1527 | 0.02 |
| 356.20 | 486  | 0.01 |
| 357.15 | 389  | 0.00 |
| 357.95 | 320  | 0.00 |
| 358.90 | 84   | 0.00 |
| 360.15 | 335  | 0.00 |
| 361.10 | 44   | 0.00 |
| 362.10 | 34   | 0.00 |
| 363.10 | 46   | 0.00 |
| 364.10 | 66   | 0.00 |
| 365.10 | 65   | 0.00 |
| 366.10 | 79   | 0.00 |
| 367.10 | 55   | 0.00 |
| 368.10 | 134  | 0.00 |
| 369.10 | 113  | 0.00 |
| 370.10 | 119  | 0.00 |
| 371.10 | 127  | 0.00 |
| 372.10 | 60   | 0.00 |
| 373.10 | 66   | 0.00 |
| 374.10 | 39   | 0.00 |
| 375.10 | 30   | 0.00 |
| 376.10 | 55   | 0.00 |
| 377.10 | 49   | 0.00 |
| 378.10 | 54   | 0.00 |
| 379.10 | 49   | 0.00 |
| 380.10 | 38   | 0.00 |
| 381.10 | 70   | 0.00 |
| 382.10 | 55   | 0.00 |
| 383.10 | 130  | 0.00 |
| 384.10 | 68   | 0.00 |
| 385.10 | 174  | 0.00 |
| 386.10 | 57   | 0.00 |
| 387.05 | 376  | 0.00 |
| 450.20 | 63   | 0.00 |

### 2.3.2. GC-MS Analysis of Raw Reaction Mixture by Using 1,1-diphenylethene as Radical Inhibitor

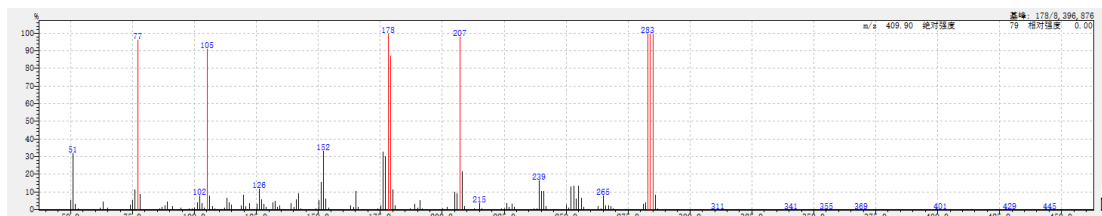


Chemical Formula: C<sub>21</sub>H<sub>16</sub>O  
 Exact Mass: 284.1201  
 Molecular Weight: 284.3580

Spectra of GC-MS



MS Spectra of the peak at 13.65 min



#### [MS Spectrum]

# of Peaks 400

Raw Spectrum 13.650 (scan : 1931)

Background No Background Spectrum

Base Peak m/z 178.15 (Inten : 8,396,876)

Event# 1

| m/z   | Absolute Intensity | Relative Intensity |
|-------|--------------------|--------------------|
| 50.05 | 454303             | 5.41               |
| 51.00 | 2693826            | 32.08              |
| 52.00 | 281726             | 3.36               |
| 53.00 | 668220.80          |                    |
| 54.05 | 3690               | 0.04               |
| 55.00 | 166630.20          |                    |
| 56.10 | 1886               | 0.02               |
| 57.05 | 3645               | 0.04               |
| 58.05 | 642                | 0.01               |
| 59.00 | 748                | 0.01               |
| 60.05 | 761                | 0.01               |
| 61.05 | 9136               | 0.11               |
| 62.05 | 973351.16          |                    |
| 63.00 | 384706             | 4.58               |
| 64.00 | 507420.60          |                    |
| 65.00 | 109732             | 1.31               |
| 66.05 | 9241               | 0.11               |
| 67.15 | 3025               | 0.04               |
| 68.15 | 2848               | 0.03               |
| 69.20 | 6102               | 0.07               |
| 70.15 | 1773               | 0.02               |
| 71.10 | 2570               | 0.03               |
| 72.05 | 816                | 0.01               |

---

|        |           |       |
|--------|-----------|-------|
| 73.05  | 194360.23 |       |
| 74.00  | 239489    | 2.85  |
| 75.00  | 461734    | 5.50  |
| 76.05  | 963603    | 11.48 |
| 77.00  | 8106030   | 96.54 |
| 78.00  | 738977    | 8.80  |
| 79.00  | 435020.52 |       |
| 79.95  | 5512      | 0.07  |
| 81.05  | 114390.14 |       |
| 81.95  | 126110.15 |       |
| 83.05  | 9831      | 0.12  |
| 83.95  | 182790.22 |       |
| 85.05  | 116910.14 |       |
| 86.00  | 704870.84 |       |
| 87.00  | 160897    | 1.92  |
| 88.05  | 207843    | 2.48  |
| 89.00  | 389238    | 4.64  |
| 89.95  | 350700.42 |       |
| 91.05  | 179962    | 2.14  |
| 92.05  | 170880.20 |       |
| 93.55  | 535570.64 |       |
| 94.45  | 952481.13 |       |
| 95.45  | 137100.16 |       |
| 96.45  | 4062      | 0.05  |
| 97.05  | 5681      | 0.07  |
| 98.00  | 686740.82 |       |
| 99.05  | 769550.92 |       |
| 100.05 | 119700    | 1.43  |
| 101.05 | 364453    | 4.34  |
| 102.05 | 685997    | 8.17  |
| 103.05 | 329953    | 3.93  |
| 104.05 | 125334    | 1.49  |
| 105.05 | 7679291   | 91.45 |
| 106.05 | 668549    | 7.96  |
| 107.35 | 170684    | 2.03  |
| 108.25 | 586120.70 |       |
| 109.25 | 109910.13 |       |
| 110.05 | 228980.27 |       |
| 111.10 | 398250.47 |       |
| 112.15 | 106393    | 1.27  |
| 113.05 | 566340    | 6.74  |
| 114.05 | 356389    | 4.24  |
| 115.00 | 266025    | 3.17  |
| 116.00 | 312020.37 |       |
| 116.80 | 4497      | 0.05  |
| 117.85 | 310750.37 |       |
| 118.85 | 214229    | 2.55  |
| 119.75 | 730479    | 8.70  |
| 120.75 | 178803    | 2.13  |
| 122.10 | 319103    | 3.80  |
| 123.05 | 377310.45 |       |
| 124.15 | 372310.44 |       |

---

|        |           |       |
|--------|-----------|-------|
| 125.15 | 272384    | 3.24  |
| 126.10 | 1006098   | 11.98 |
| 127.05 | 490032    | 5.84  |
| 128.05 | 297773    | 3.55  |
| 129.05 | 156962    | 1.87  |
| 130.55 | 400550.48 |       |
| 131.55 | 355041    | 4.23  |
| 132.50 | 448678    | 5.34  |
| 133.45 | 161459    | 1.92  |
| 134.30 | 224369    | 2.67  |
| 135.25 | 392200.47 |       |
| 136.10 | 3454      | 0.04  |
| 137.05 | 537440.64 |       |
| 138.15 | 539020.64 |       |
| 139.10 | 333396    | 3.97  |
| 140.15 | 150592    | 1.79  |
| 141.10 | 505366    | 6.02  |
| 142.10 | 791550    | 9.43  |
| 143.05 | 669000.80 |       |
| 144.05 | 864       | 0.01  |
| 145.05 | 731       | 0.01  |
| 146.05 | 2046      | 0.02  |
| 147.05 | 5166      | 0.06  |
| 148.15 | 4037      | 0.05  |
| 149.15 | 607170.72 |       |
| 150.10 | 483295    | 5.76  |
| 151.10 | 1338497   | 15.94 |
| 152.10 | 2820070   | 33.58 |
| 153.05 | 545024    | 6.49  |
| 154.05 | 101989    | 1.21  |
| 155.05 | 122050.15 |       |
| 156.10 | 1209      | 0.01  |
| 157.05 | 446       | 0.01  |
| 158.05 | 464       | 0.01  |
| 159.05 | 736       | 0.01  |
| 160.05 | 413       | 0.00  |
| 161.05 | 135870.16 |       |
| 162.05 | 397840.47 |       |
| 163.05 | 208138    | 2.48  |
| 164.15 | 150694    | 1.79  |
| 165.05 | 889574    | 10.59 |
| 166.05 | 132615    | 1.58  |
| 167.05 | 304960.36 |       |
| 168.10 | 6774      | 0.08  |
| 169.15 | 1287      | 0.02  |
| 169.80 | 310       | 0.00  |
| 170.85 | 427       | 0.01  |
| 172.15 | 369       | 0.00  |
| 173.15 | 5920      | 0.07  |
| 174.05 | 782420.93 |       |
| 175.15 | 216184    | 2.57  |
| 176.05 | 2773030   | 33.02 |

---

|        |           |        |
|--------|-----------|--------|
| 177.15 | 2561507   | 30.51  |
| 178.15 | 8396876   | 100.00 |
| 179.10 | 7332876   | 87.33  |
| 180.05 | 985737    | 11.74  |
| 181.05 | 205873    | 2.45   |
| 182.00 | 258120.31 |        |
| 182.95 | 2533      | 0.03   |
| 184.05 | 413       | 0.00   |
| 185.05 | 3118      | 0.04   |
| 186.05 | 7738      | 0.09   |
| 187.05 | 552780.66 |        |
| 188.05 | 497000.59 |        |
| 189.05 | 297439    | 3.54   |
| 190.10 | 985611.17 |        |
| 191.05 | 459698    | 5.47   |
| 192.05 | 842411.00 |        |
| 193.05 | 360910.43 |        |
| 194.05 | 6288      | 0.07   |
| 195.15 | 1007      | 0.01   |
| 196.05 | 242       | 0.00   |
| 197.05 | 1077      | 0.01   |
| 198.00 | 7076      | 0.08   |
| 199.05 | 105690.13 |        |
| 200.05 | 610740.73 |        |
| 201.05 | 458540.55 |        |
| 202.05 | 149275    | 1.78   |
| 203.05 | 443940.53 |        |
| 204.05 | 208540.25 |        |
| 205.05 | 857597    | 10.21  |
| 206.05 | 789510    | 9.40   |
| 207.05 | 8246043   | 98.20  |
| 208.05 | 1821972   | 21.70  |
| 209.00 | 178193    | 2.12   |
| 210.00 | 132810.16 |        |
| 211.00 | 185350.22 |        |
| 212.05 | 128090.15 |        |
| 213.00 | 889881.06 |        |
| 214.05 | 314750.37 |        |
| 215.05 | 320567    | 3.82   |
| 216.05 | 690490.82 |        |
| 217.05 | 110700.13 |        |
| 218.05 | 107130.13 |        |
| 219.10 | 5406      | 0.06   |
| 220.00 | 3844      | 0.05   |
| 221.05 | 5190      | 0.06   |
| 222.05 | 6342      | 0.08   |
| 223.05 | 9720      | 0.12   |
| 224.05 | 590350.70 |        |
| 225.05 | 553870.66 |        |
| 226.05 | 310221    | 3.69   |
| 227.05 | 155256    | 1.85   |
| 228.05 | 280483    | 3.34   |

---

|        |           |       |
|--------|-----------|-------|
| 229.05 | 139525    | 1.66  |
| 230.05 | 235820.28 |       |
| 231.00 | 103050.12 |       |
| 232.05 | 1915      | 0.02  |
| 233.05 | 684       | 0.01  |
| 234.05 | 985       | 0.01  |
| 235.05 | 6229      | 0.07  |
| 236.05 | 6983      | 0.08  |
| 237.05 | 584460.70 |       |
| 238.15 | 614140.73 |       |
| 239.05 | 1395204   | 16.62 |
| 240.05 | 914724    | 10.89 |
| 241.10 | 888258    | 10.58 |
| 242.05 | 178554    | 2.13  |
| 243.05 | 286510.34 |       |
| 244.05 | 132520.16 |       |
| 245.05 | 3412      | 0.04  |
| 246.00 | 1465      | 0.02  |
| 247.05 | 2024      | 0.02  |
| 248.05 | 207820.25 |       |
| 249.05 | 230980.28 |       |
| 250.05 | 247601    | 2.95  |
| 251.15 | 115966    | 1.38  |
| 252.05 | 1133996   | 13.50 |
| 253.05 | 1160520   | 13.82 |
| 254.05 | 534737    | 6.37  |
| 255.10 | 1153596   | 13.74 |
| 256.10 | 583854    | 6.95  |
| 257.05 | 143936    | 1.71  |
| 258.05 | 202330.24 |       |
| 259.05 | 3672      | 0.04  |
| 260.15 | 2088      | 0.02  |
| 261.10 | 180780.22 |       |
| 262.15 | 136830.16 |       |
| 263.05 | 183352    | 2.18  |
| 264.15 | 800530.95 |       |
| 265.10 | 701852    | 8.36  |
| 266.10 | 227938    | 2.71  |
| 267.10 | 211018    | 2.51  |
| 268.10 | 194886    | 2.32  |
| 269.05 | 665340.79 |       |
| 270.05 | 111930.13 |       |
| 271.05 | 1505      | 0.02  |
| 272.10 | 271       | 0.00  |
| 273.10 | 166       | 0.00  |
| 274.10 | 271       | 0.00  |
| 275.10 | 162       | 0.00  |
| 276.15 | 376       | 0.00  |
| 277.15 | 817       | 0.01  |
| 278.15 | 1847      | 0.02  |
| 279.10 | 223930.27 |       |
| 280.15 | 163730.19 |       |

---

|        |           |       |
|--------|-----------|-------|
| 281.10 | 284940    | 3.39  |
| 282.05 | 362306    | 4.31  |
| 283.05 | 8382887   | 99.83 |
| 284.00 | 8382566   | 99.83 |
| 285.00 | 8382566   | 99.83 |
| 286.05 | 734976    | 8.75  |
| 286.95 | 631740.75 |       |
| 287.95 | 4277      | 0.05  |
| 289.20 | 479       | 0.01  |
| 290.20 | 183       | 0.00  |
| 291.15 | 338       | 0.00  |
| 292.05 | 398       | 0.00  |
| 293.10 | 582       | 0.01  |
| 294.15 | 439       | 0.01  |
| 295.05 | 1631      | 0.02  |

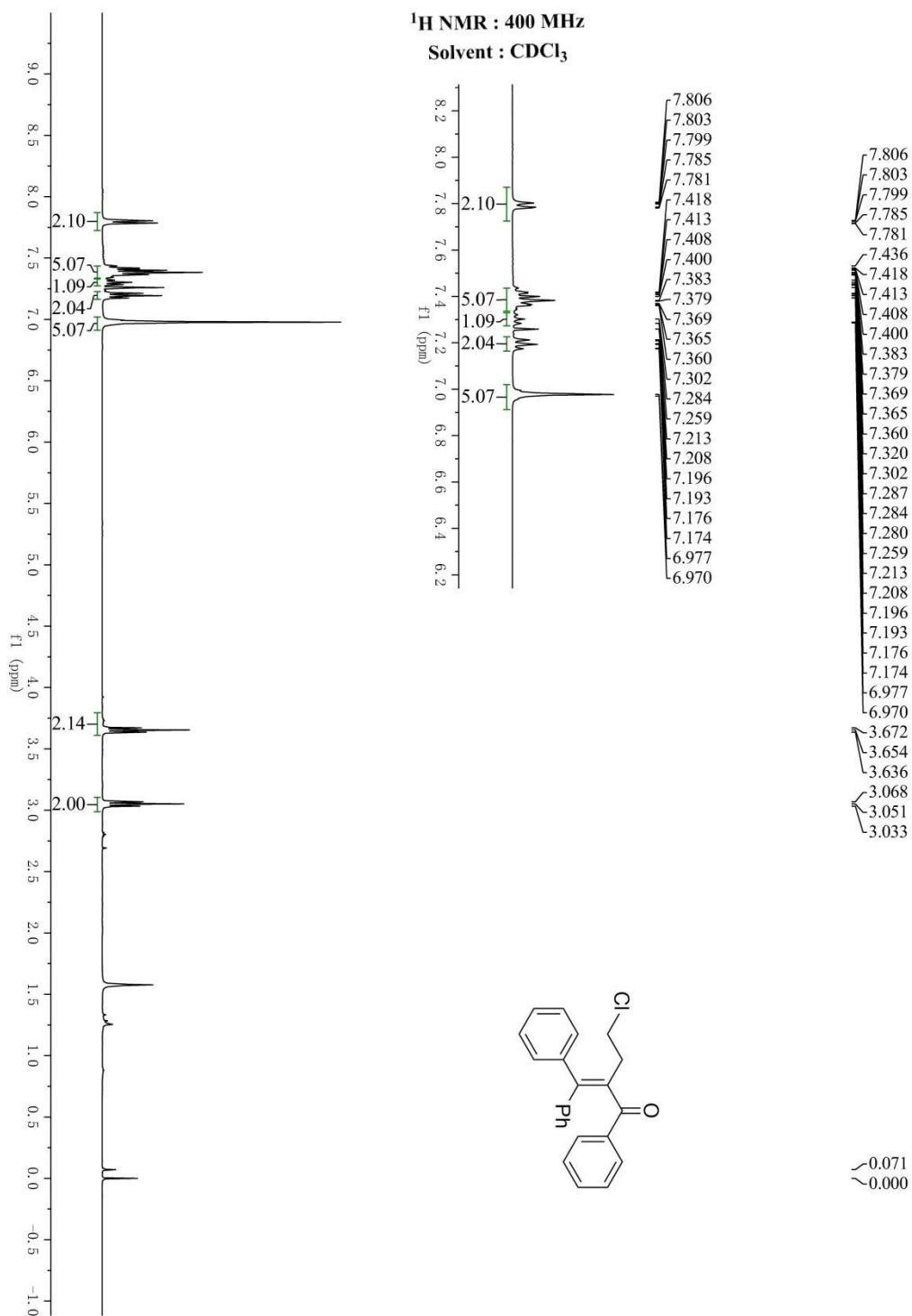
### 3. References

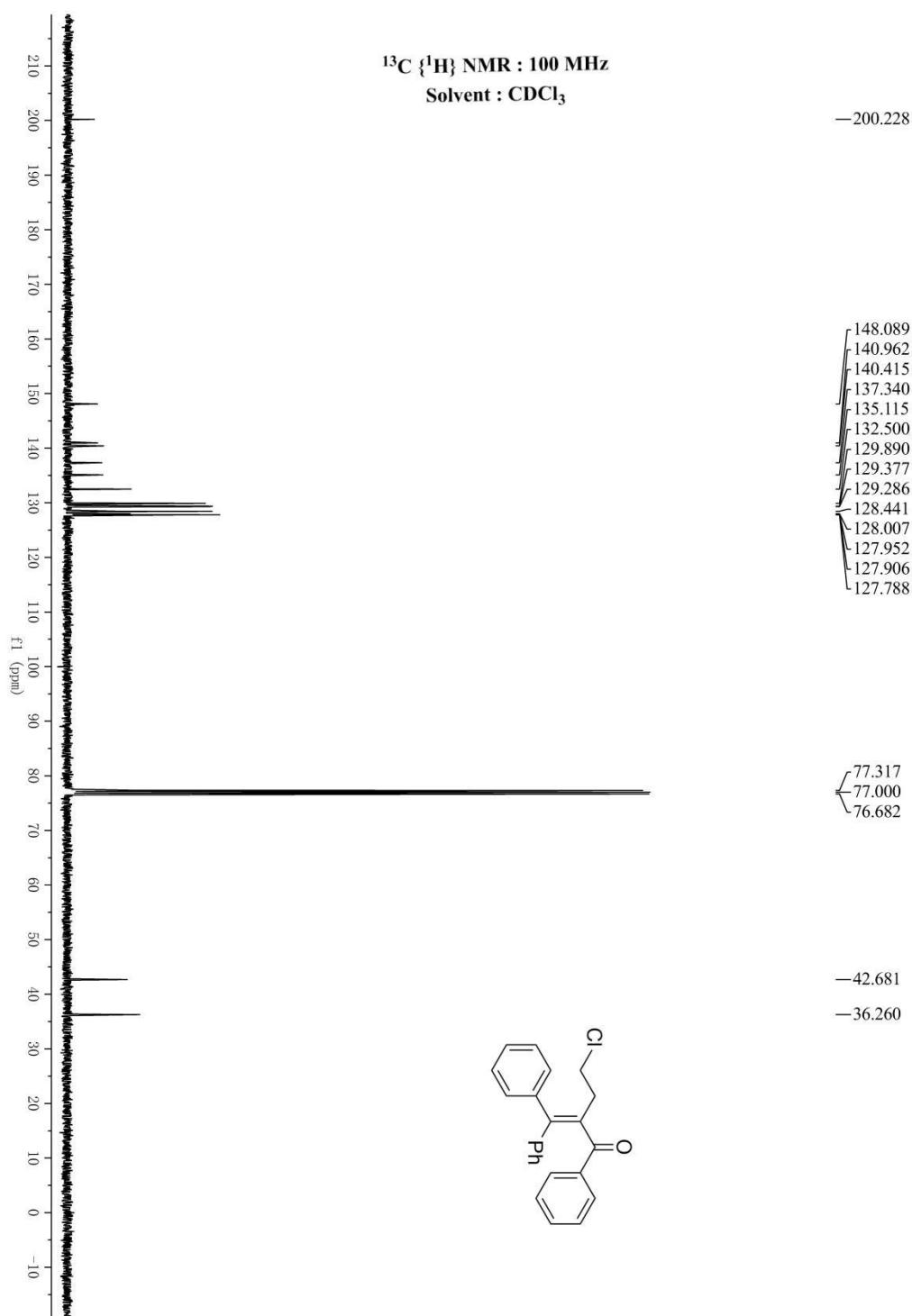
[1] Wu, D.; Fan, W.; Wu, L.; Chen, P.; Liu, G. Copper-Catalyzed Enantioselective Radical Chlorination of Alkenes. *ACS Catal.* **2022**, 12, 5284-5291

#### 4.1. H and <sup>13</sup>C spectra

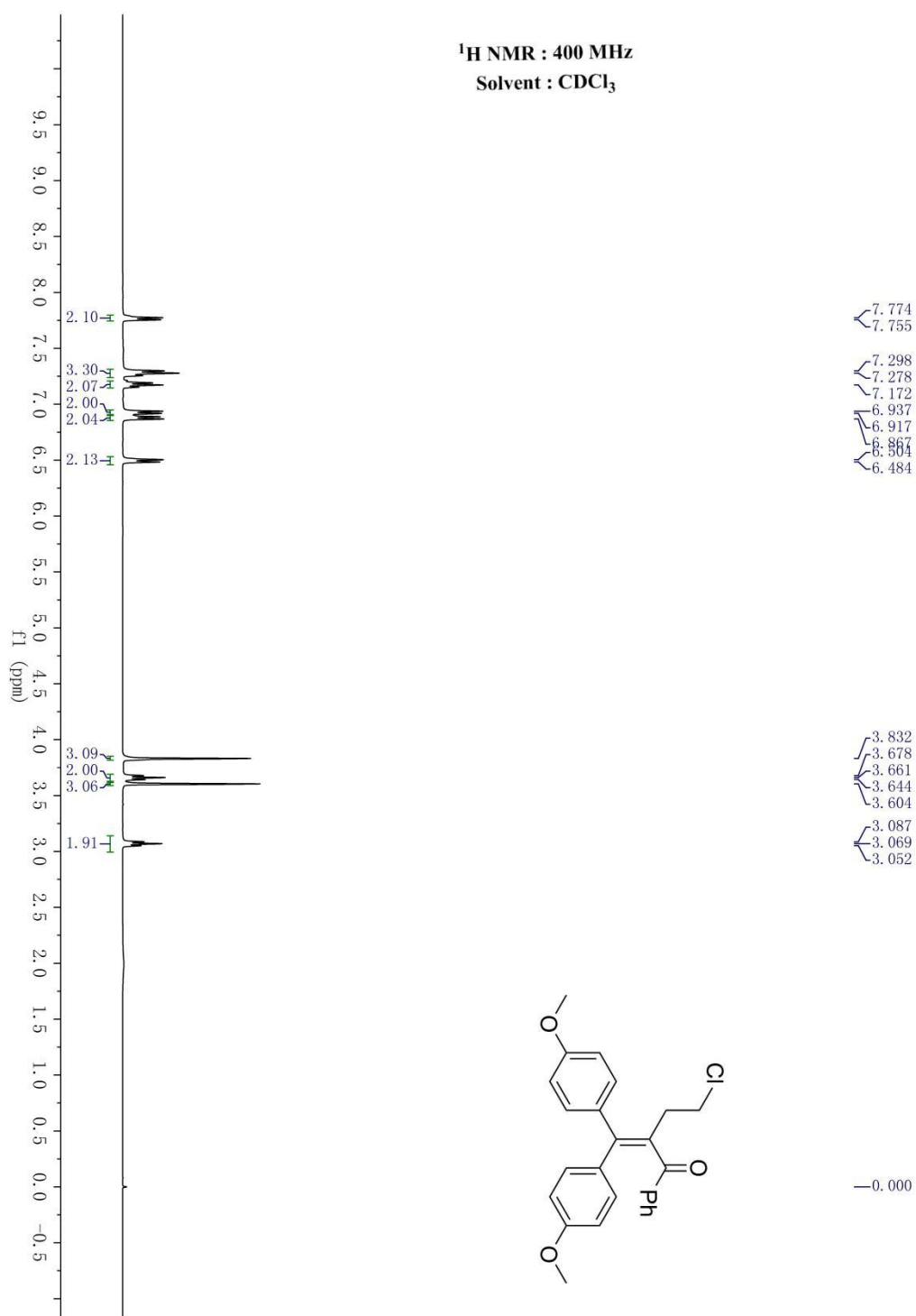
##### 4-Chloro-2-(diphenylmethylene)-1-phenylbutan-1-one (3aa)

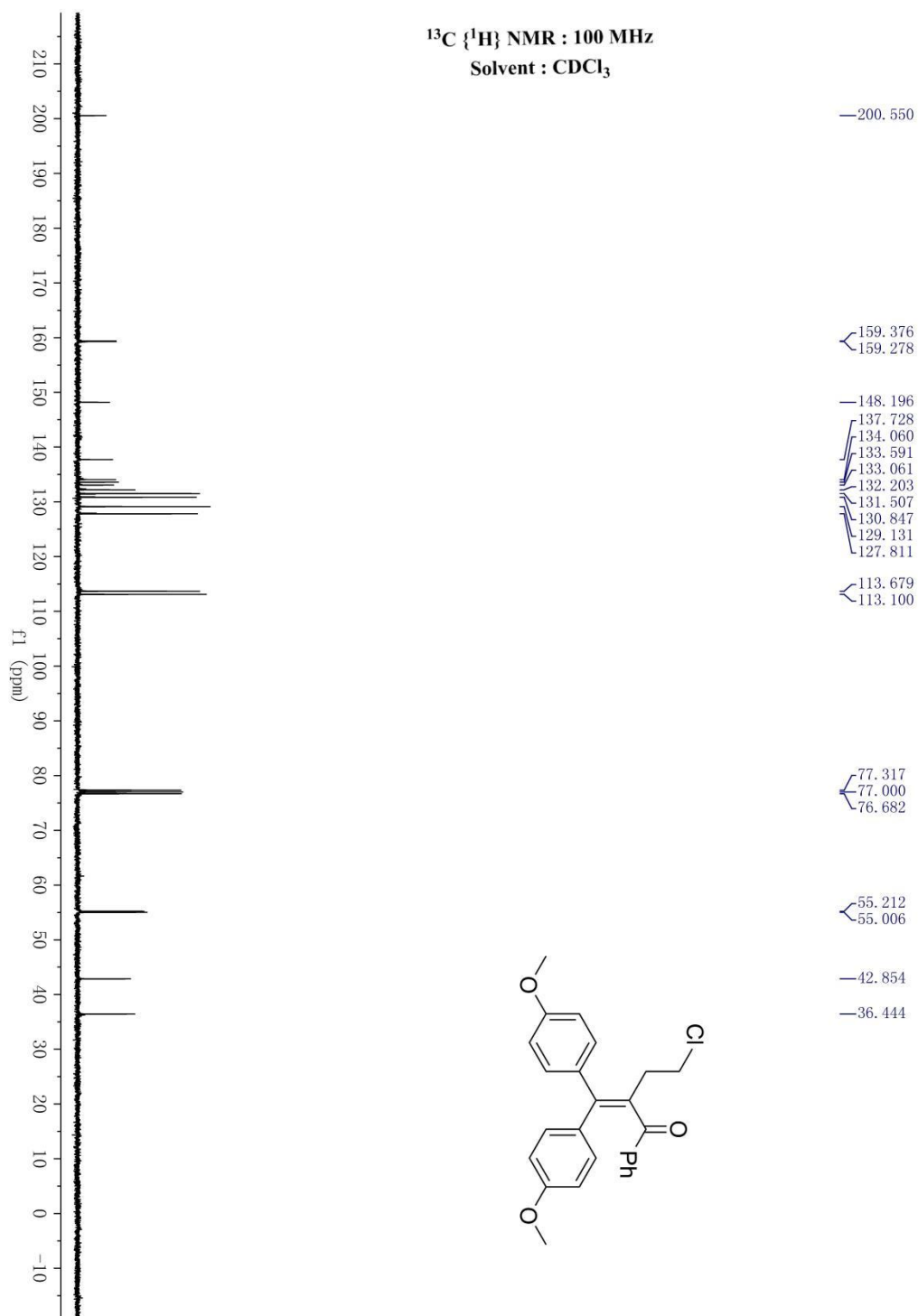




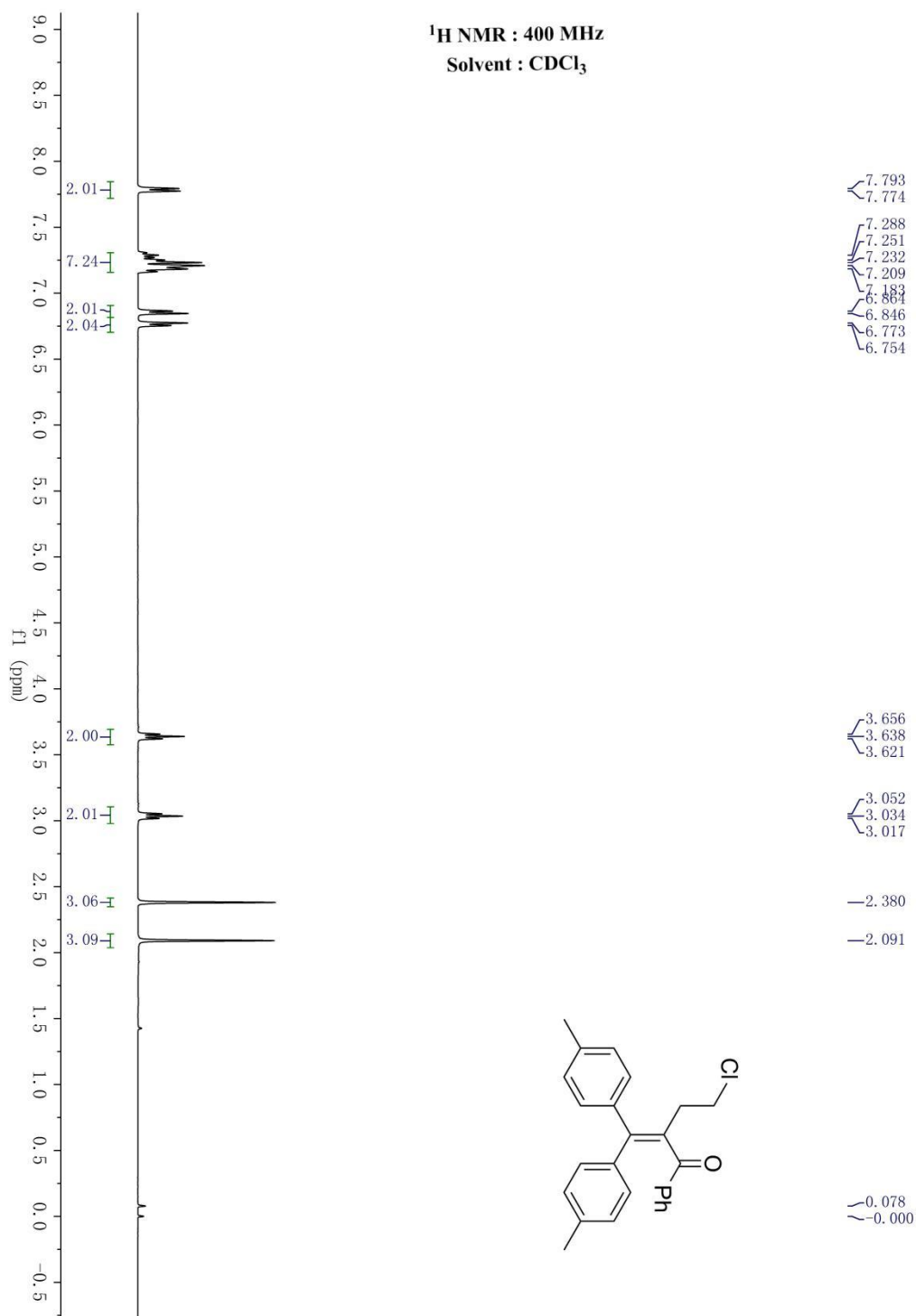


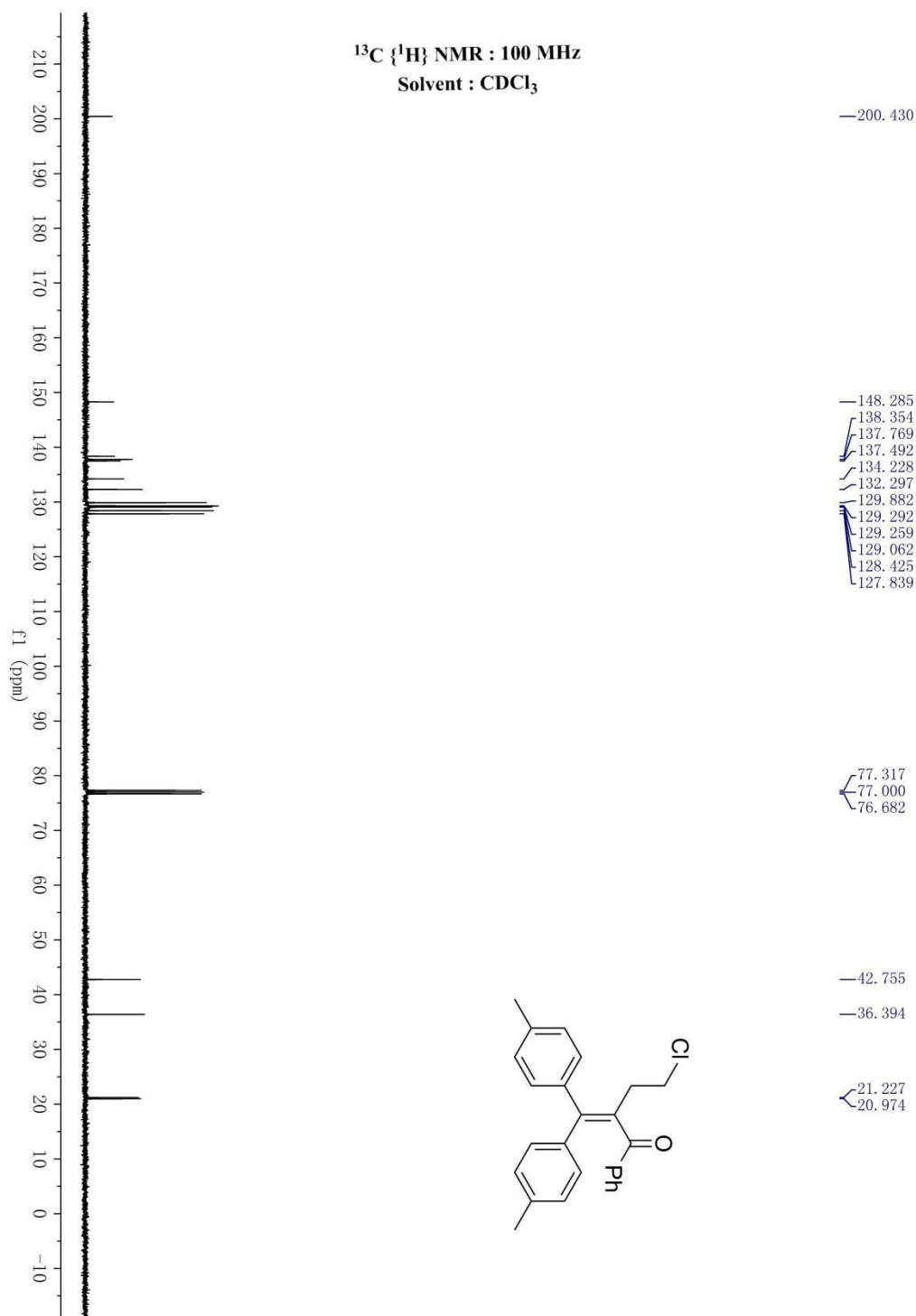
2-(bis(4-methoxyphenyl)methylene)-4-chloro-1-phenylbutan-1-one (3ba)



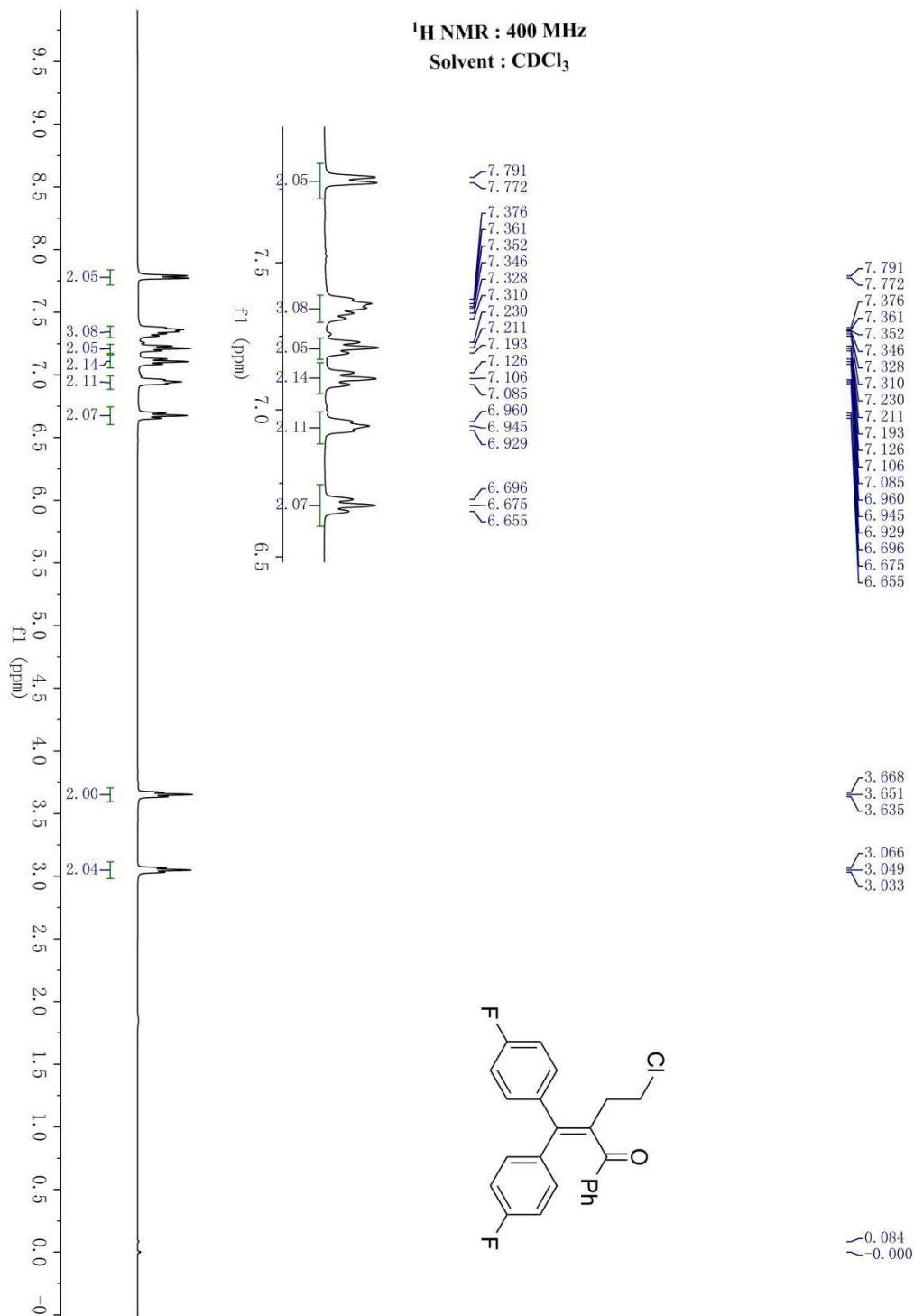


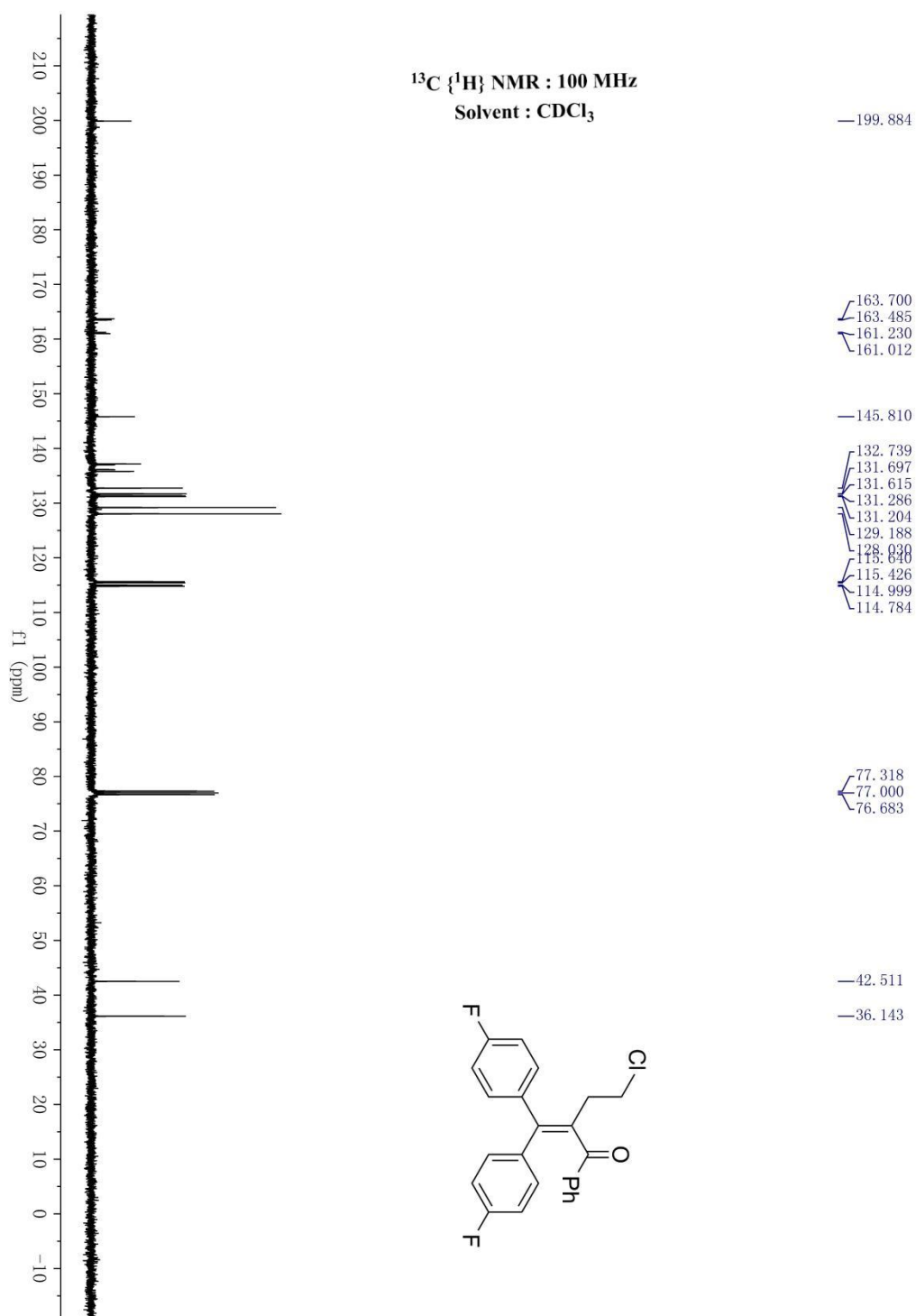
**4-Chloro-2-(di-p-tolylmethylene)-1-phenylbutan-1-one (3ca)**



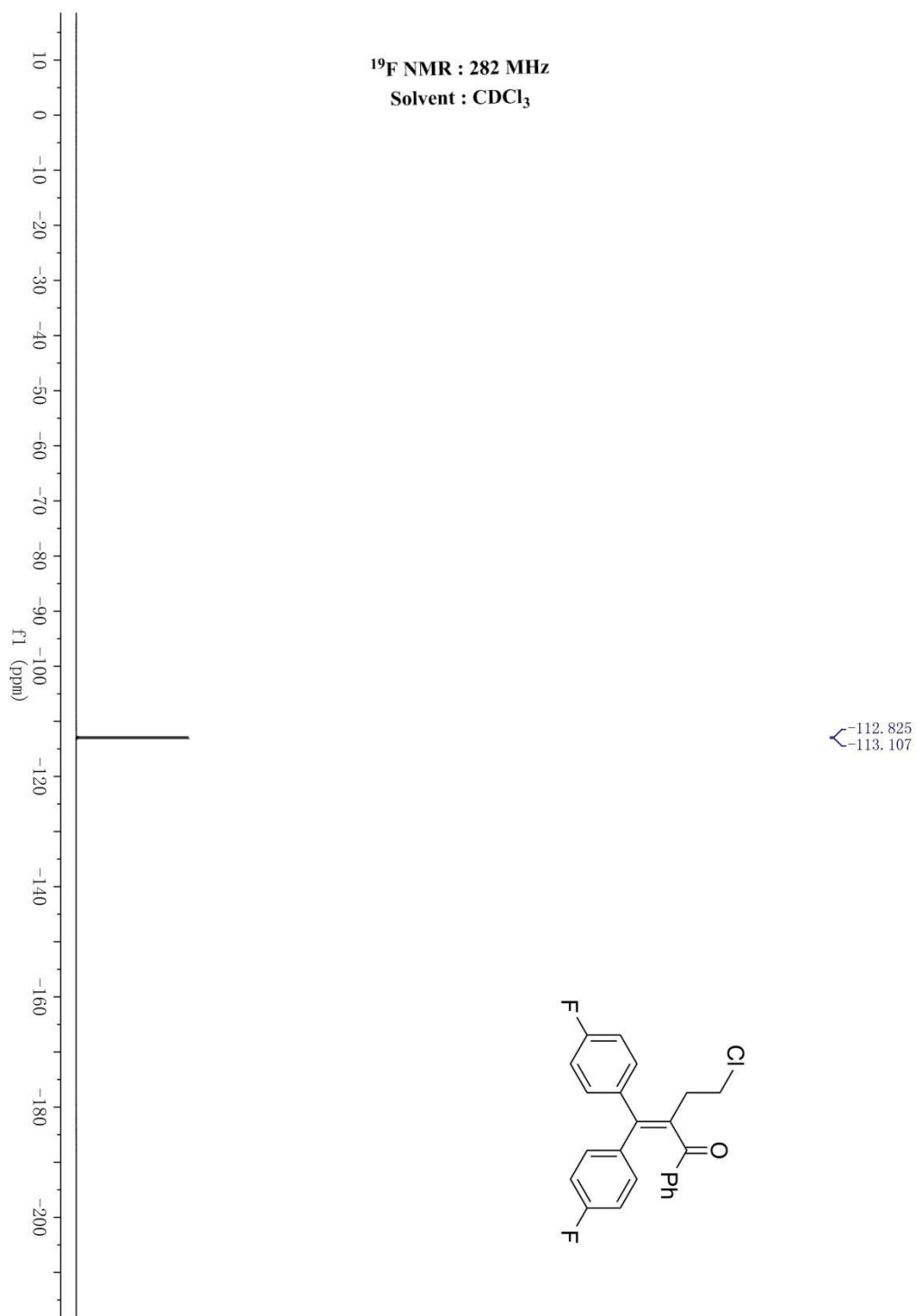


2-(Bis(4-fluorophenyl)methylene)-4-chloro-1-phenylbutan-1-one (3da)

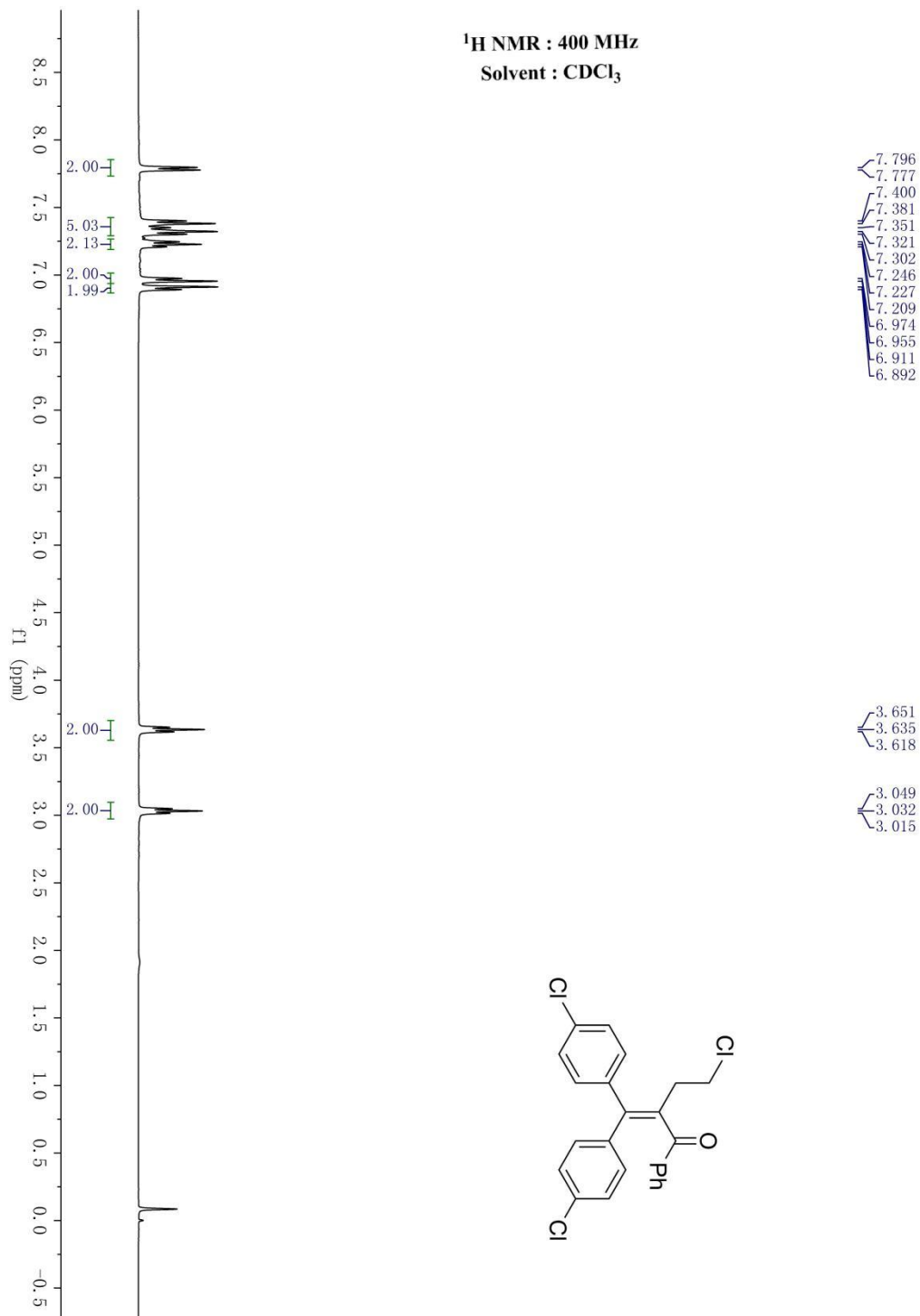


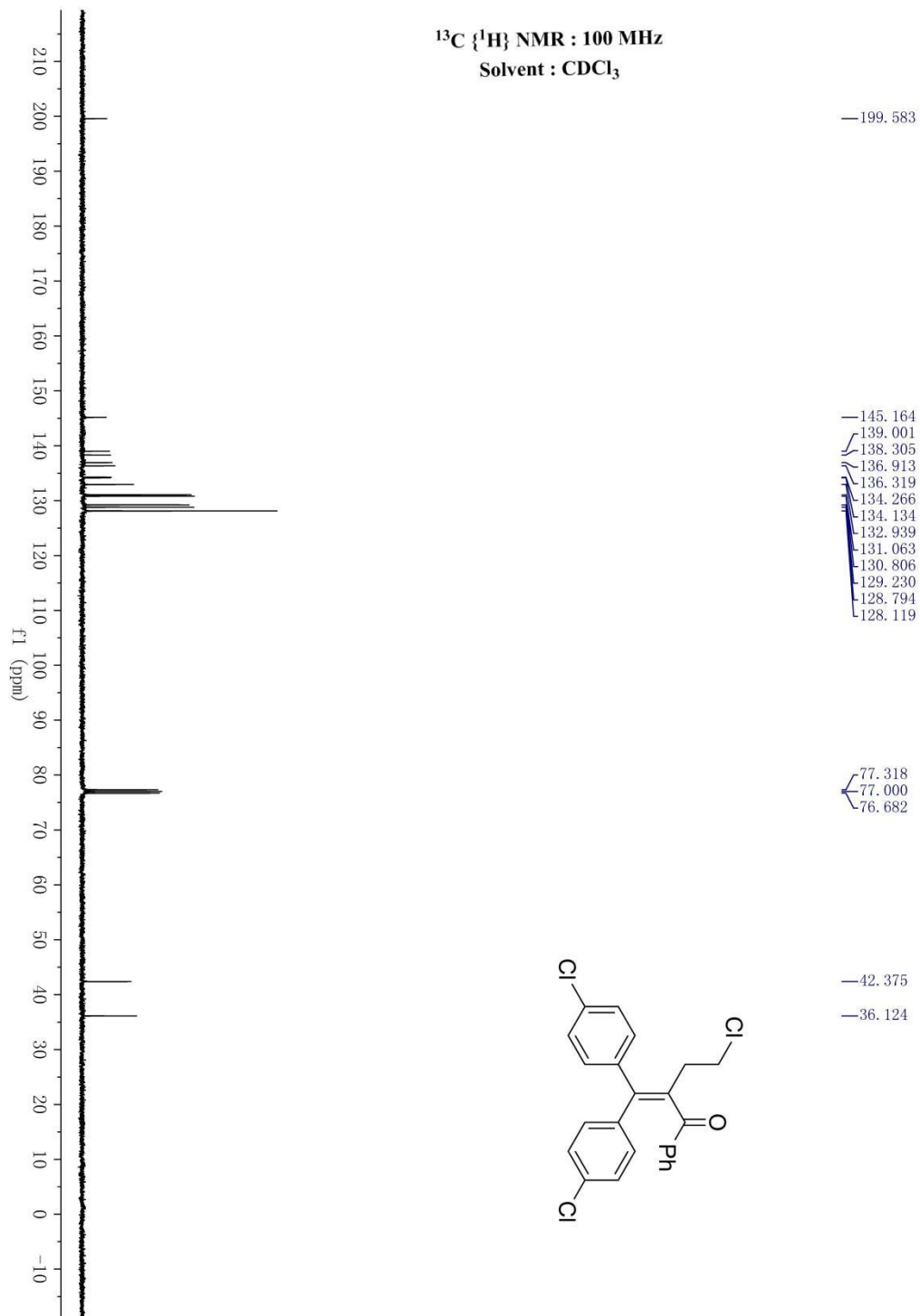




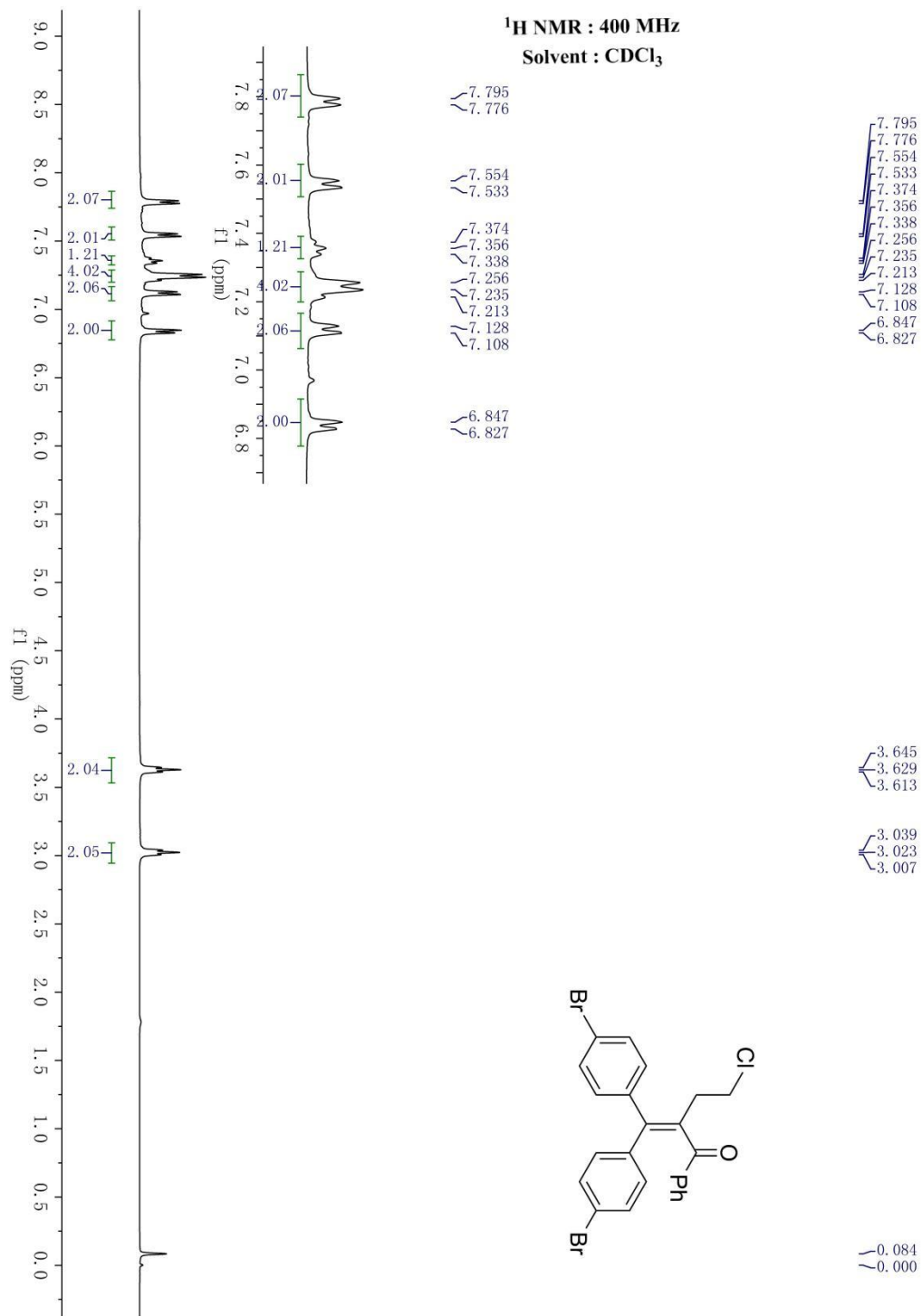


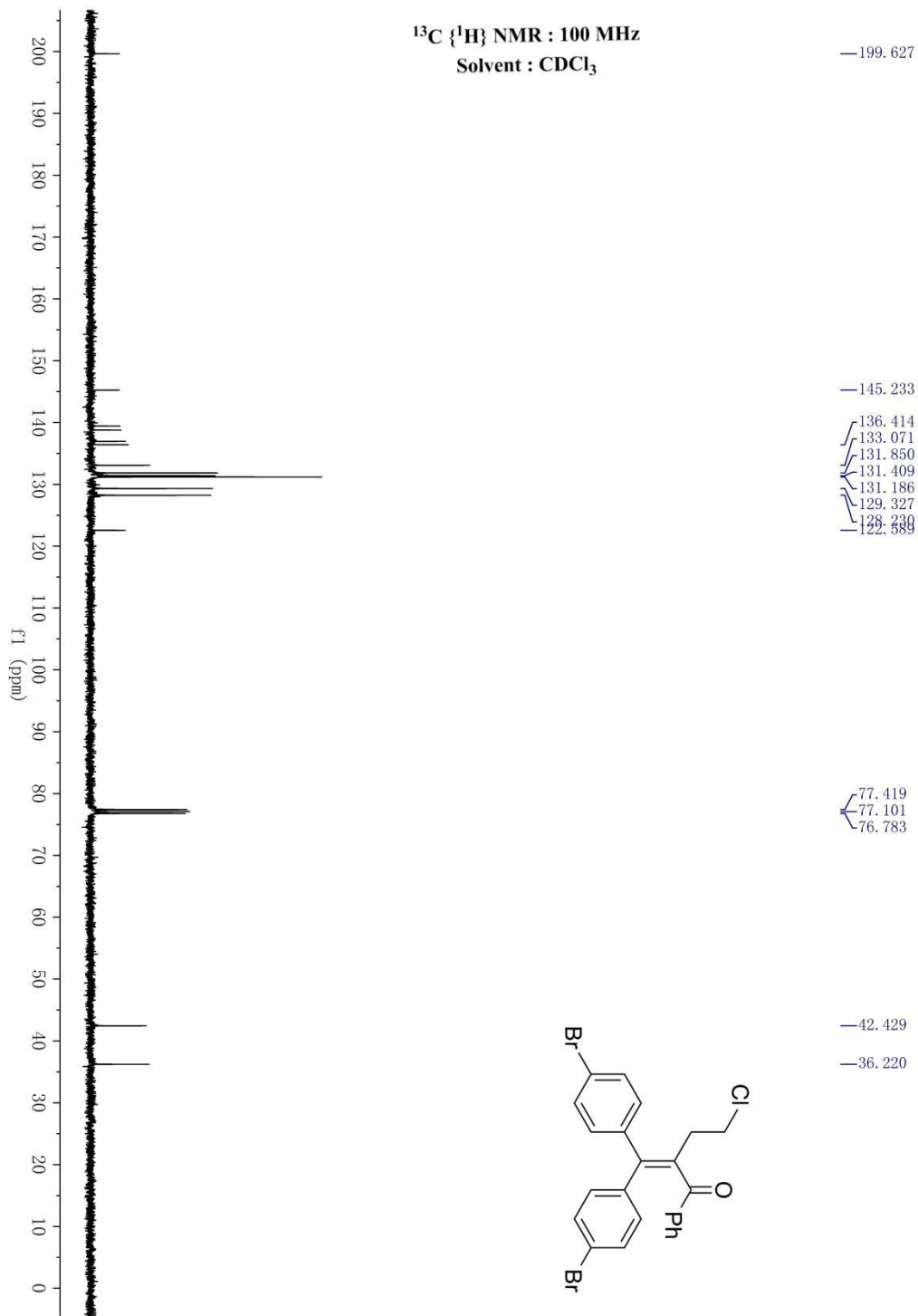
**2-(bis(4-chlorophenyl)methylene)-4-chloro-1-phenylbutan-1-one (3ea)**



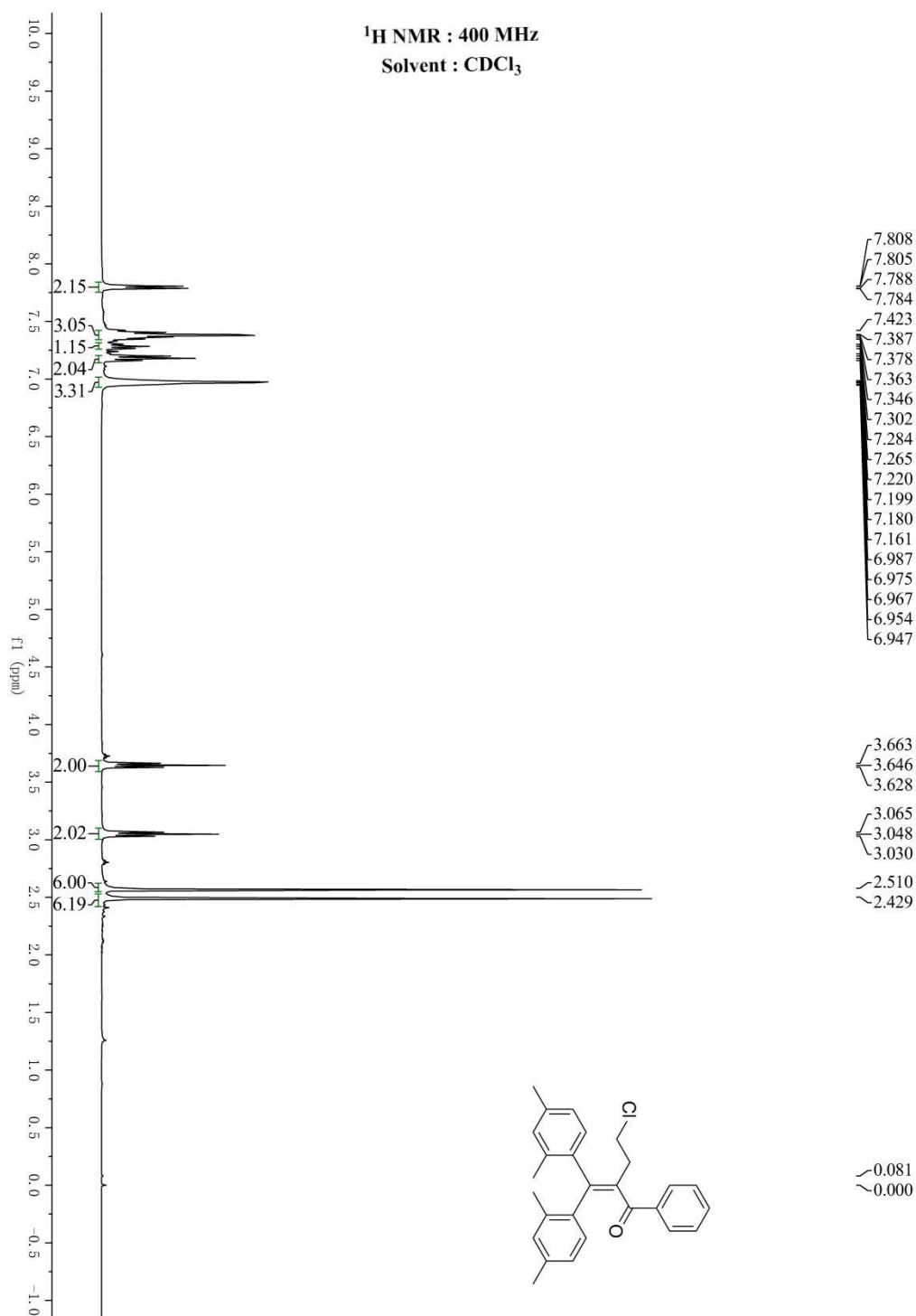


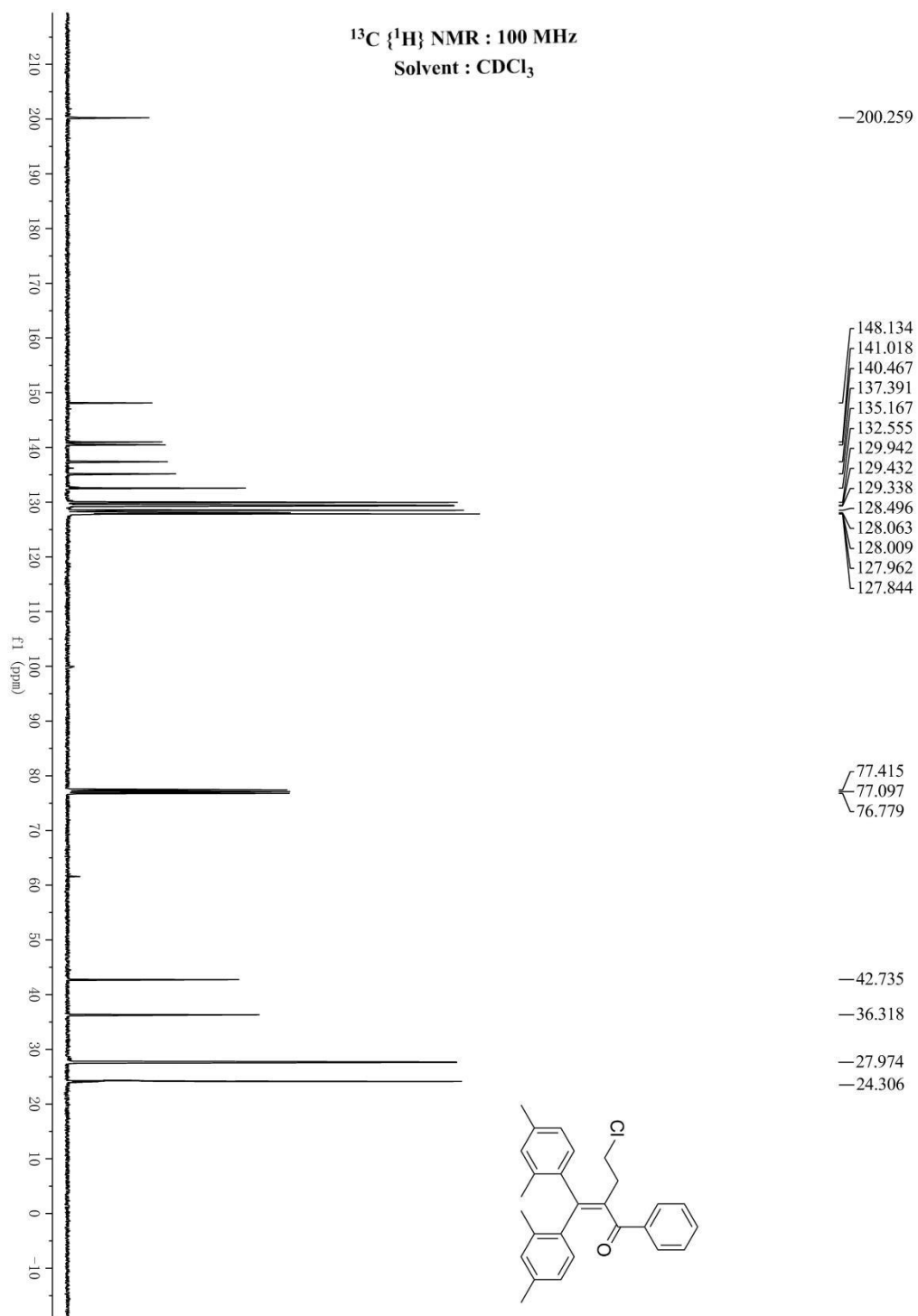
## 2-(bis(4-bromophenyl)methylene)-4-chloro-1-phenylbutan-1-one (3fa)



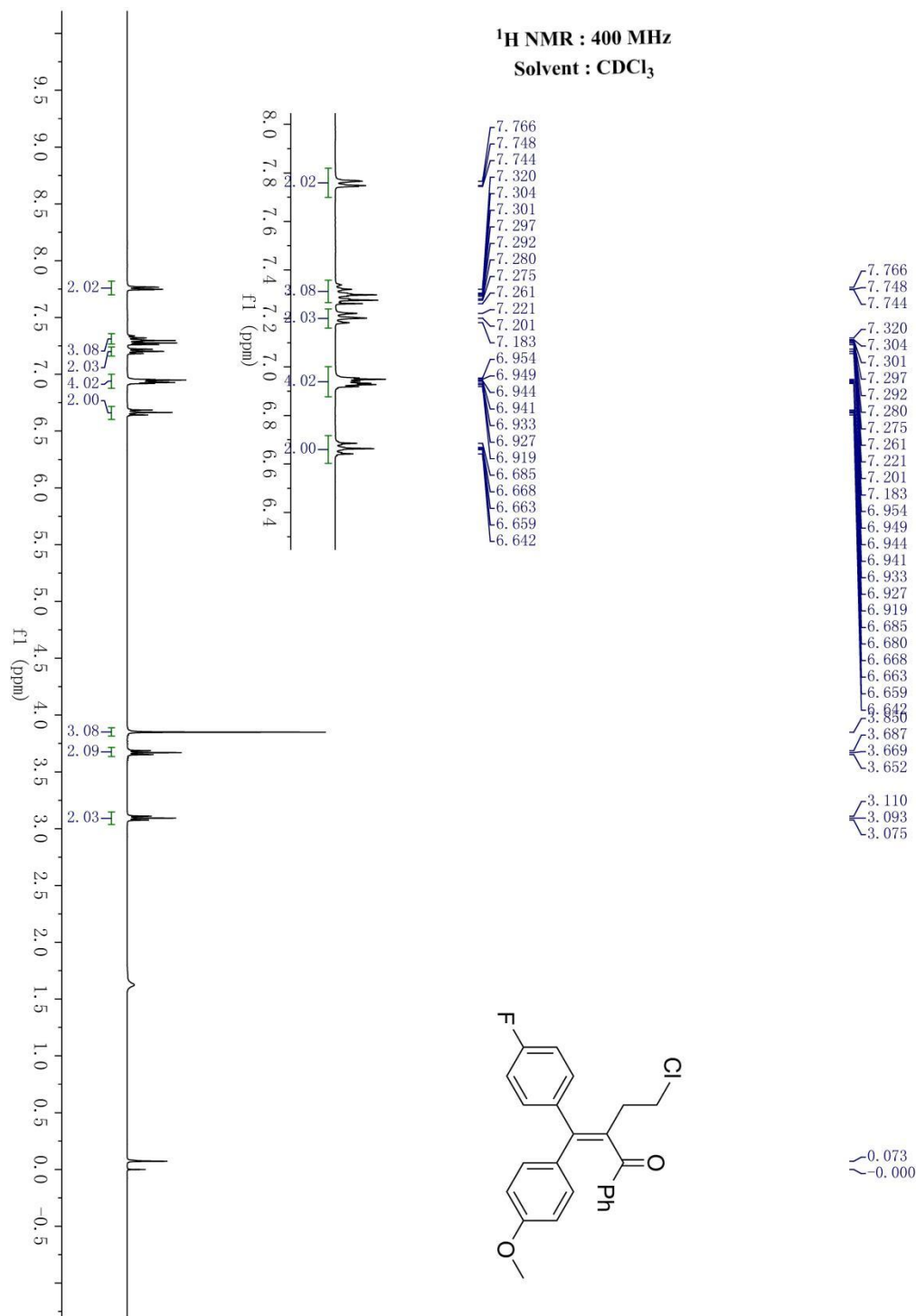


2-(bis(2,4-dimethylphenyl)methylene)-4-chloro-1-phenylbutan-1-one (3ga)

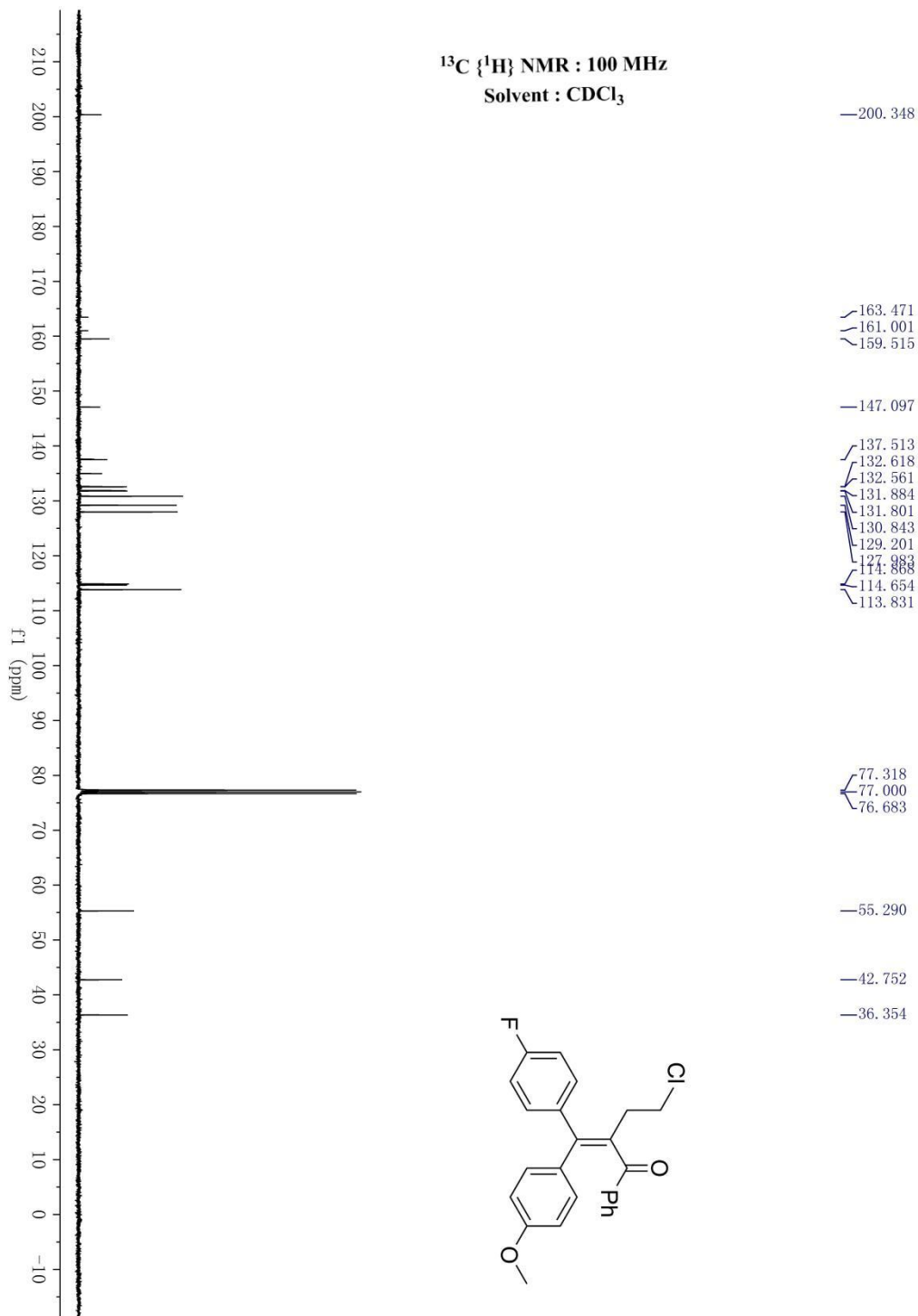


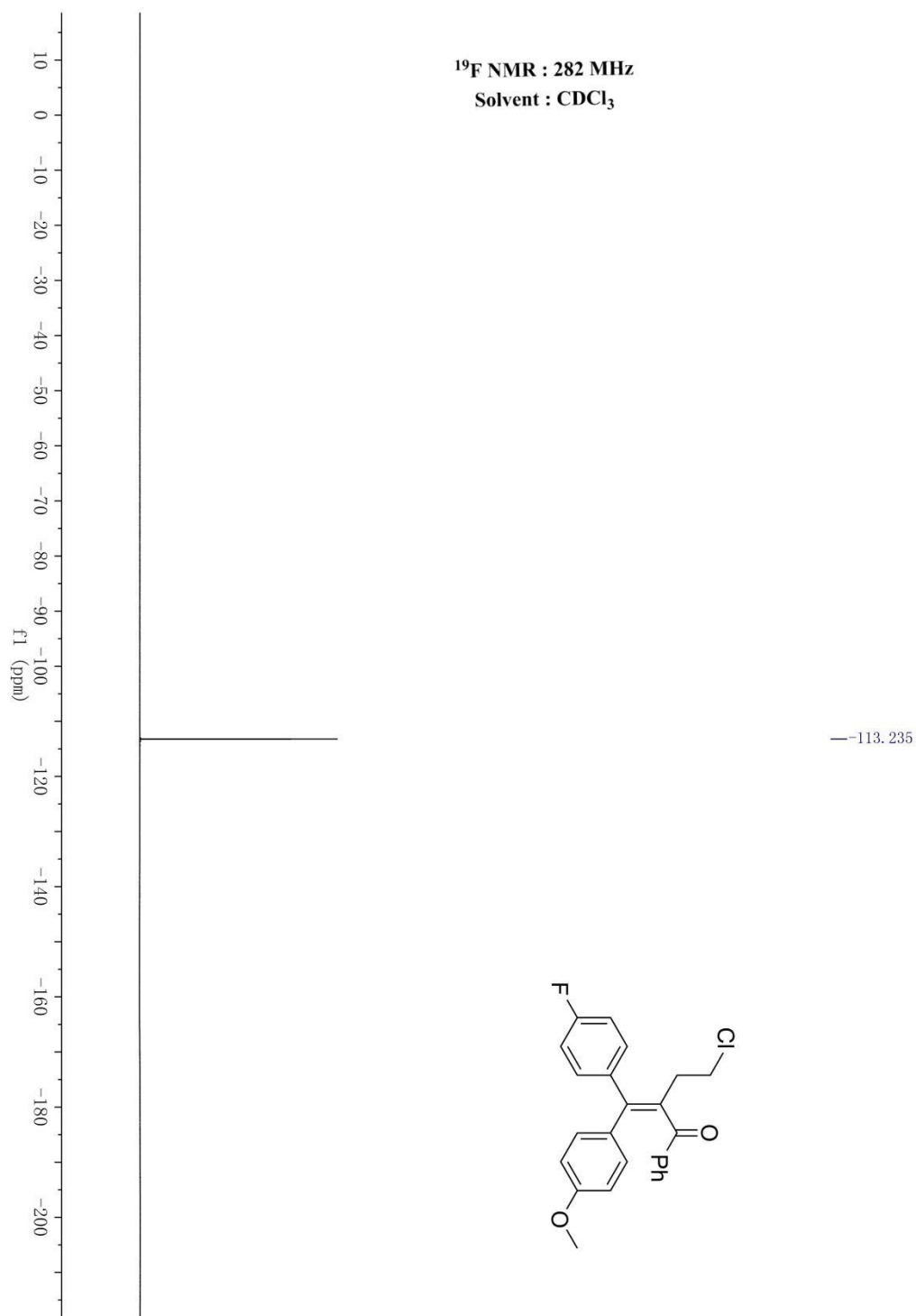


4-chloro-2-((4-fluorophenyl)(4-methoxyphenyl)methylene)-1-phenylbutan-1-one (3ha)

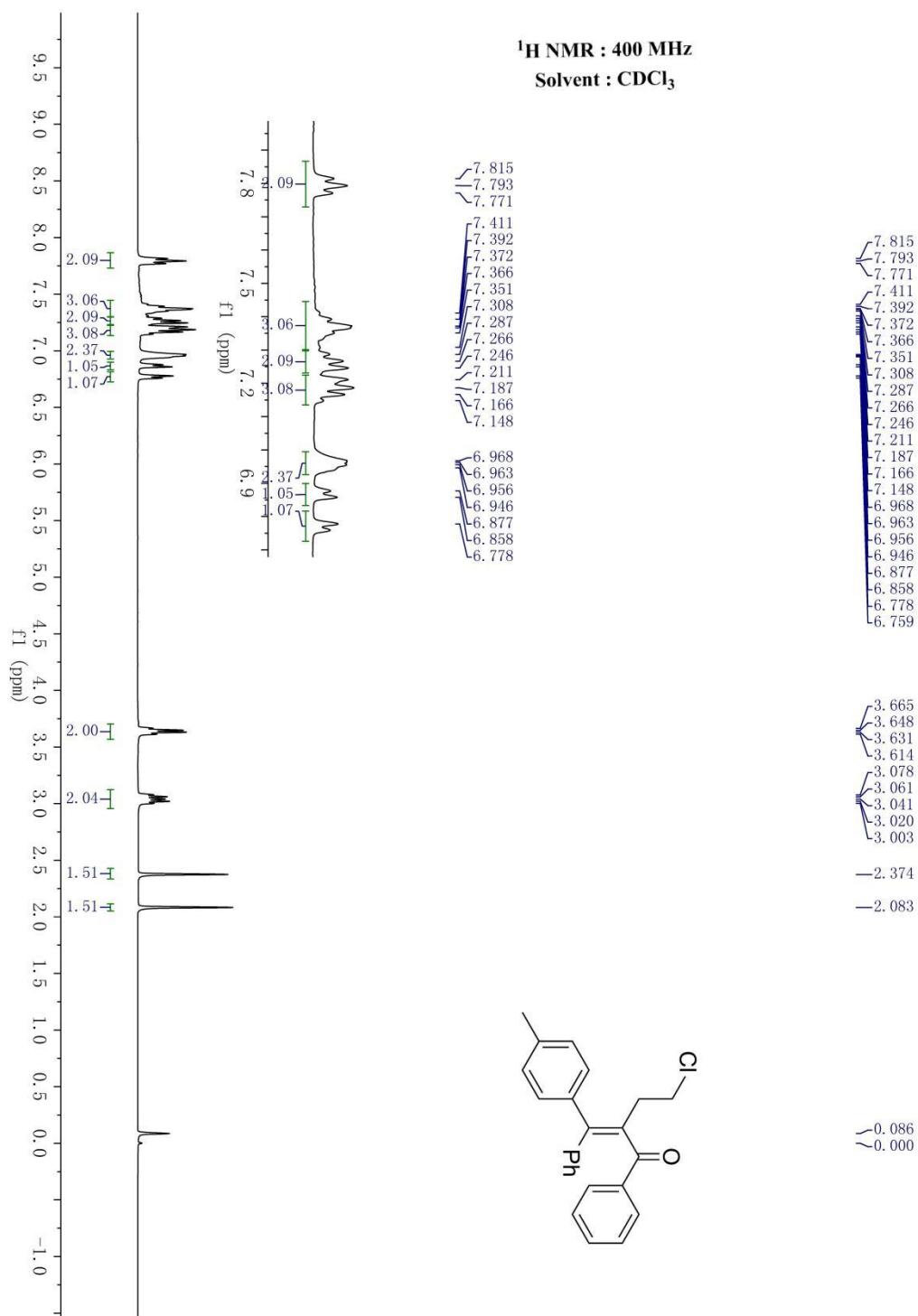


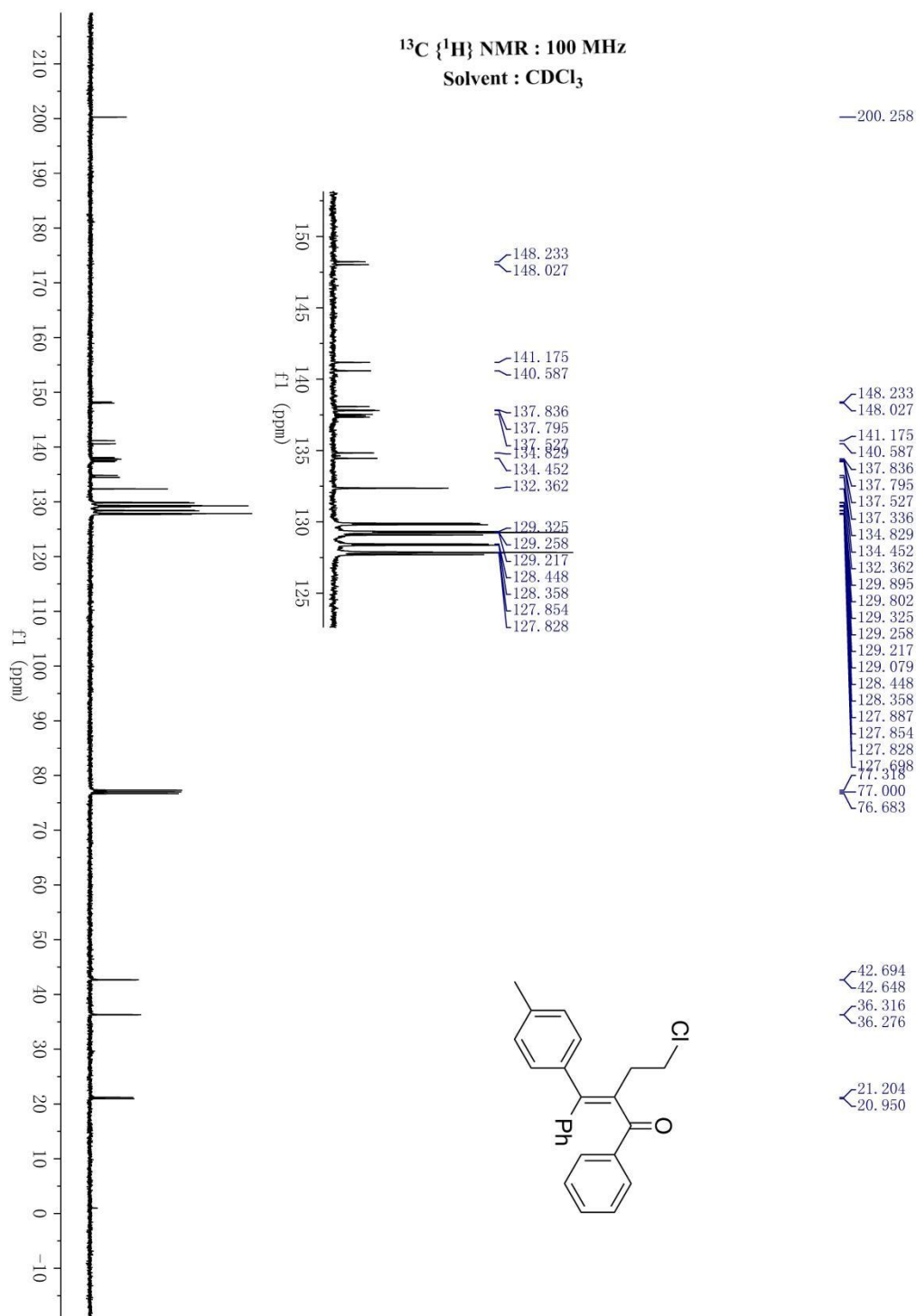




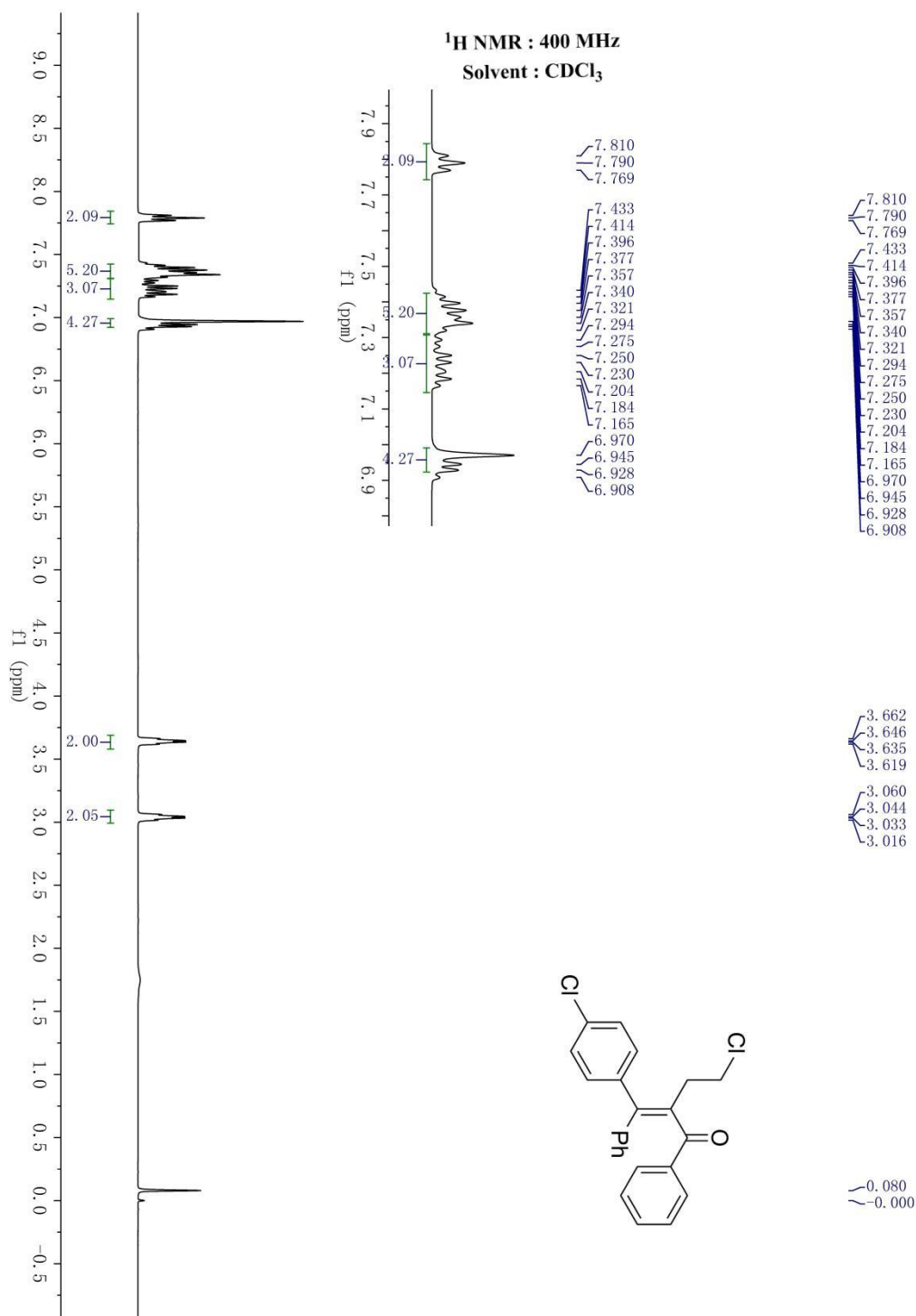


4-chloro-1-phenyl-2-(phenyl(p-tolyl)methylene)butan-1-one (3ia)

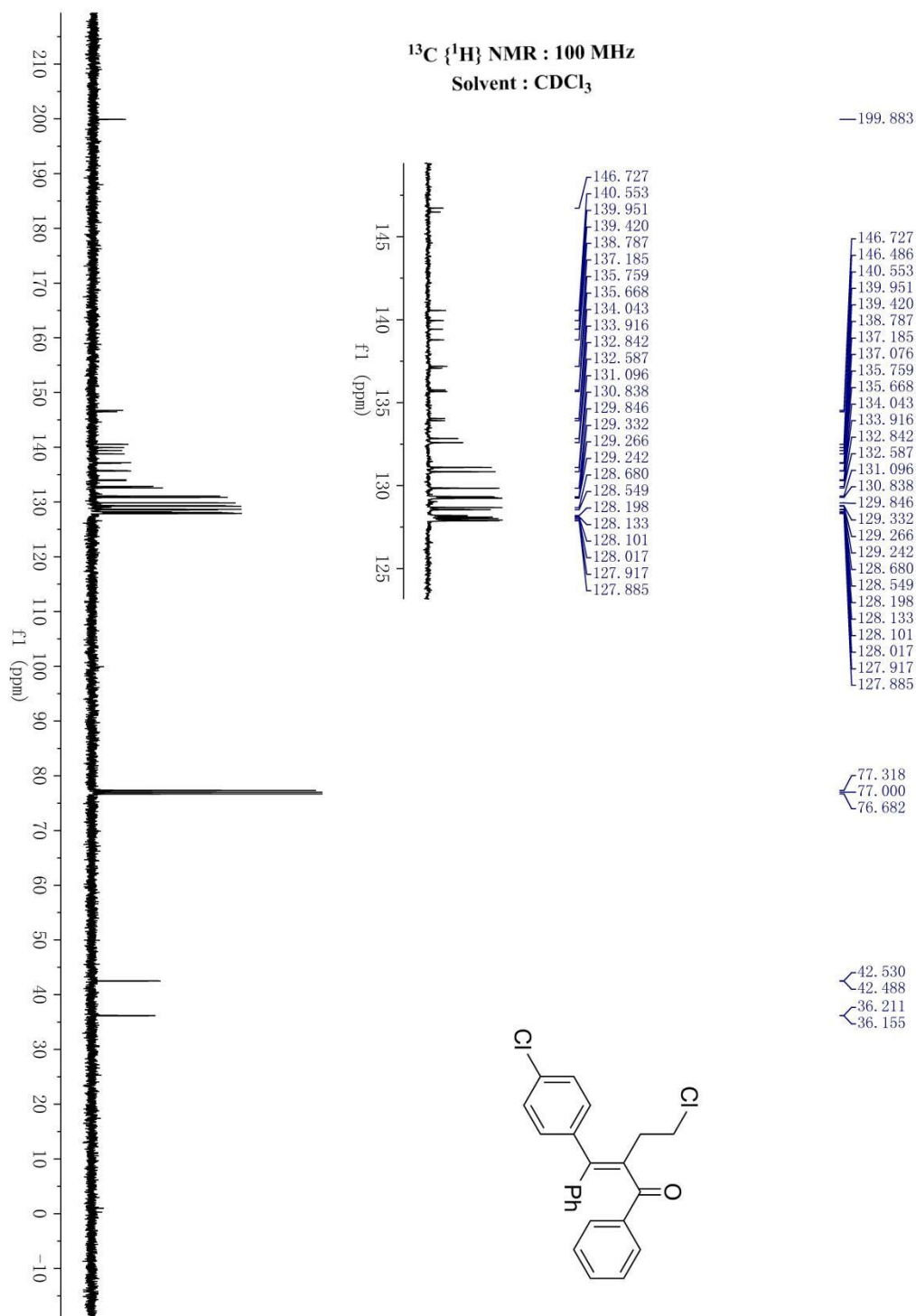




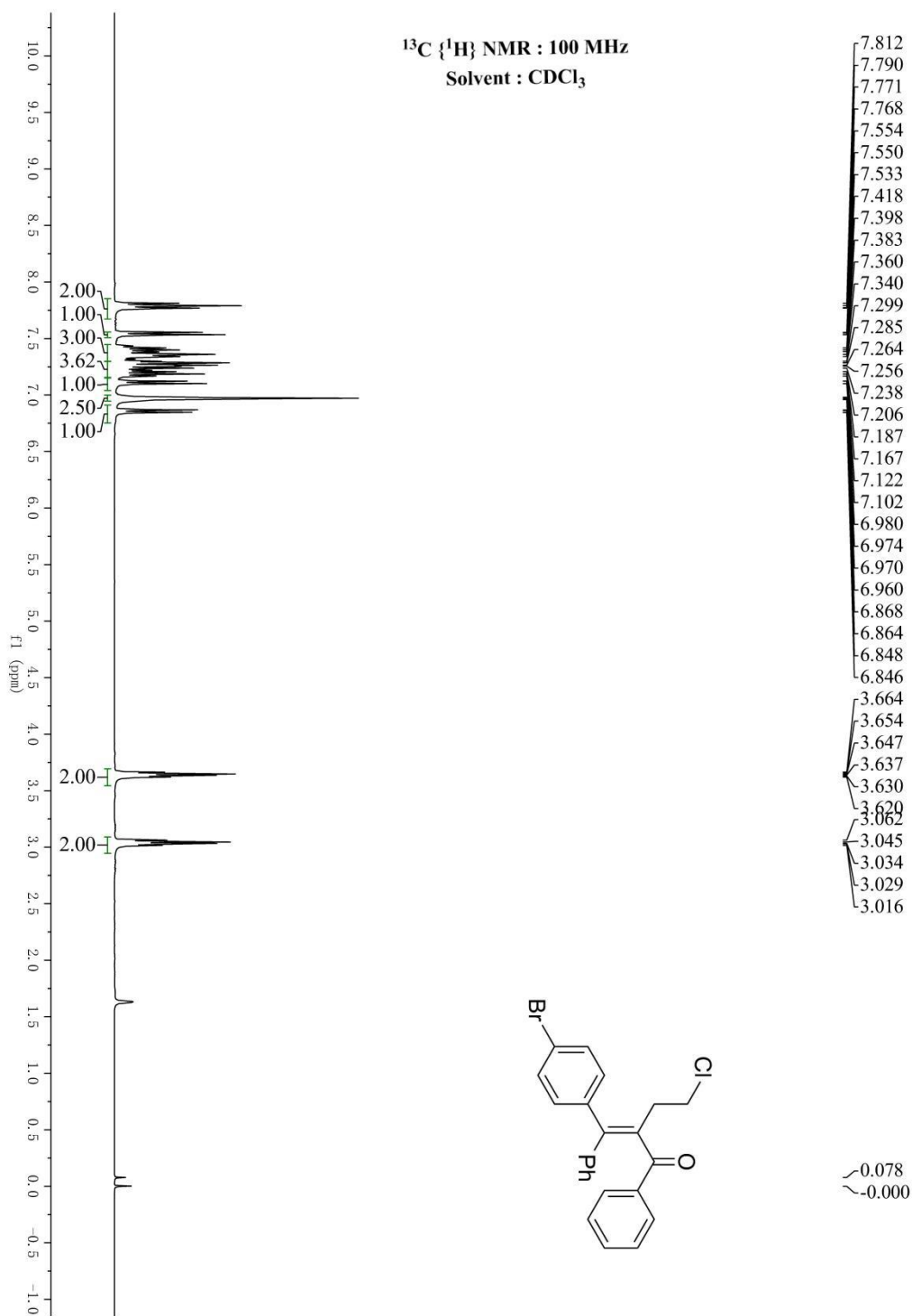
**4-Chloro-2-((4-chlorophenyl)(phenyl)methylene)-1-phenylbutan-1-one (3ja)**

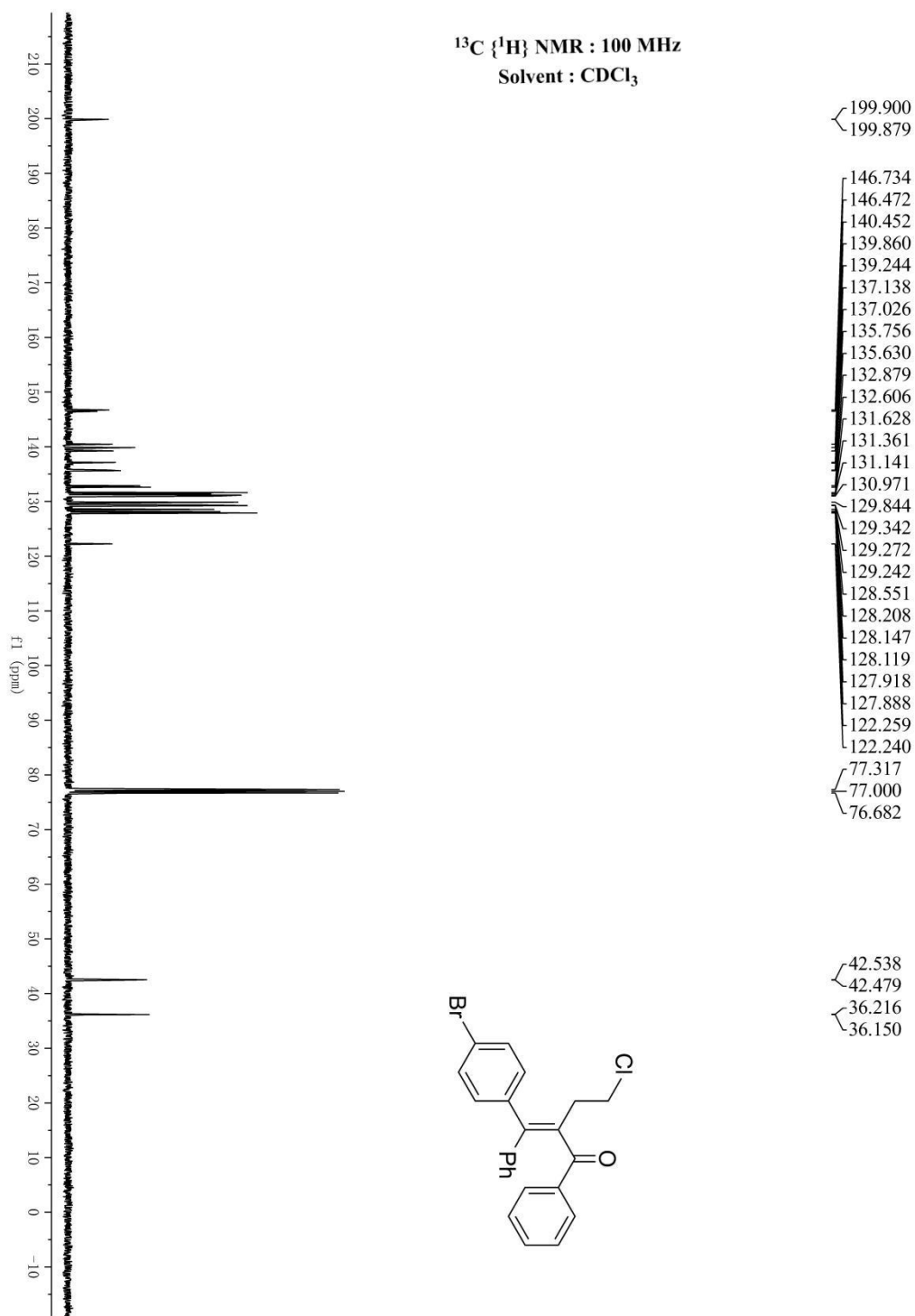


*I am running a few minutes late; my previous meeting is running over.*



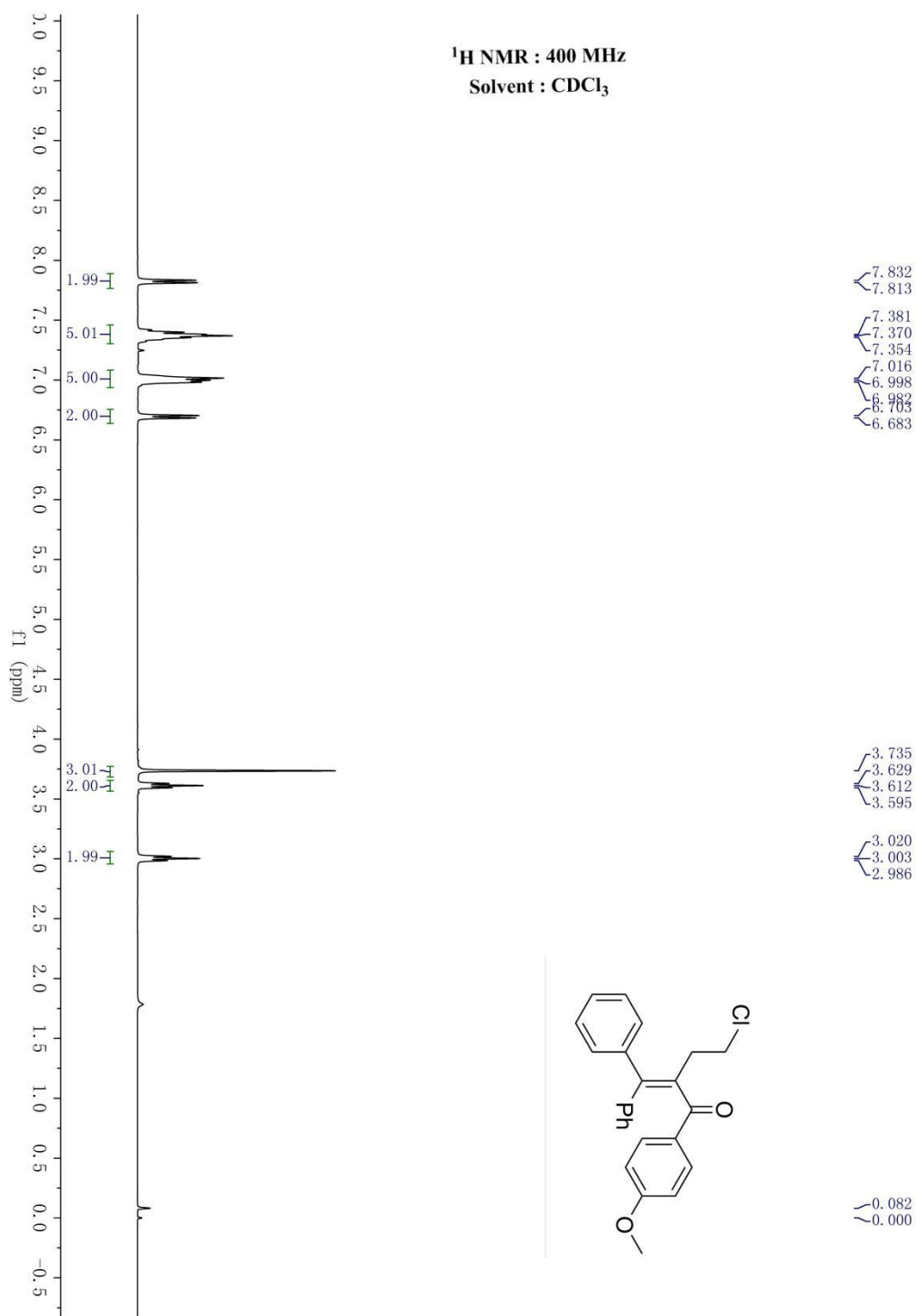
2-((4-Bromophenyl)(phenyl)methylene)-4-chloro-1-phenylbutan-1-one (3ka)

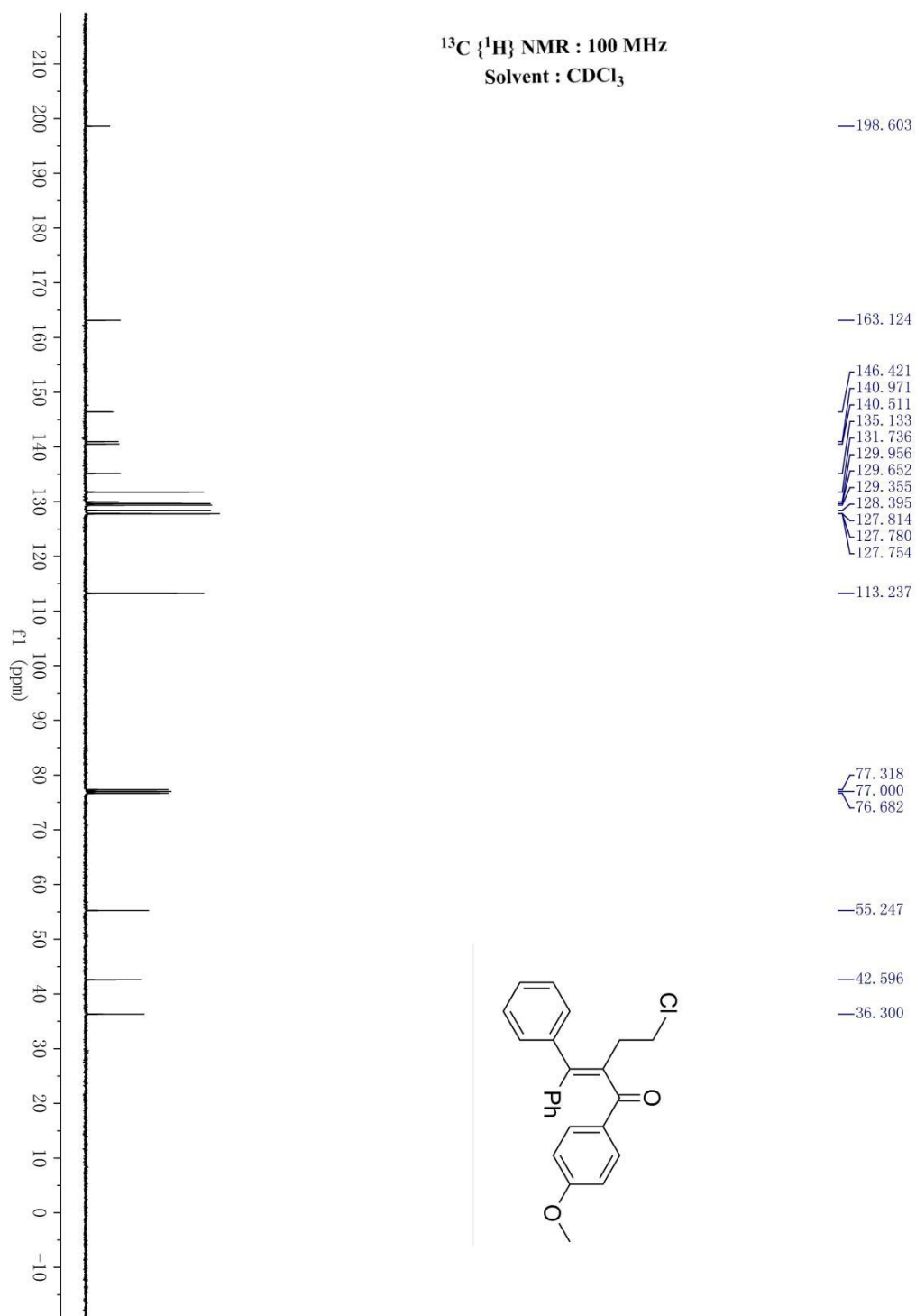




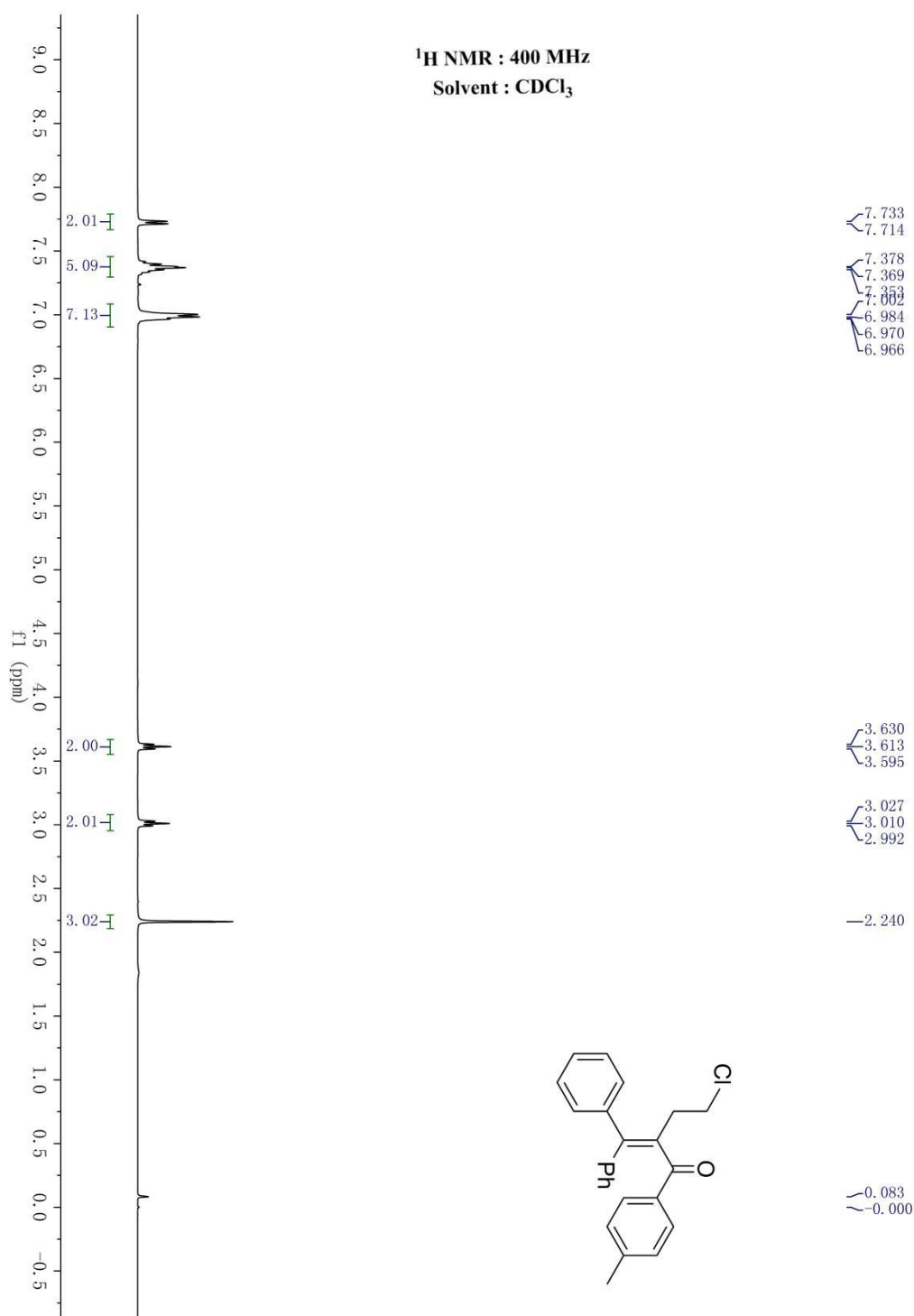
4-chloro-2-(diphenylmethylene)-1-(p-tolyl)butan-1-one (3ab)

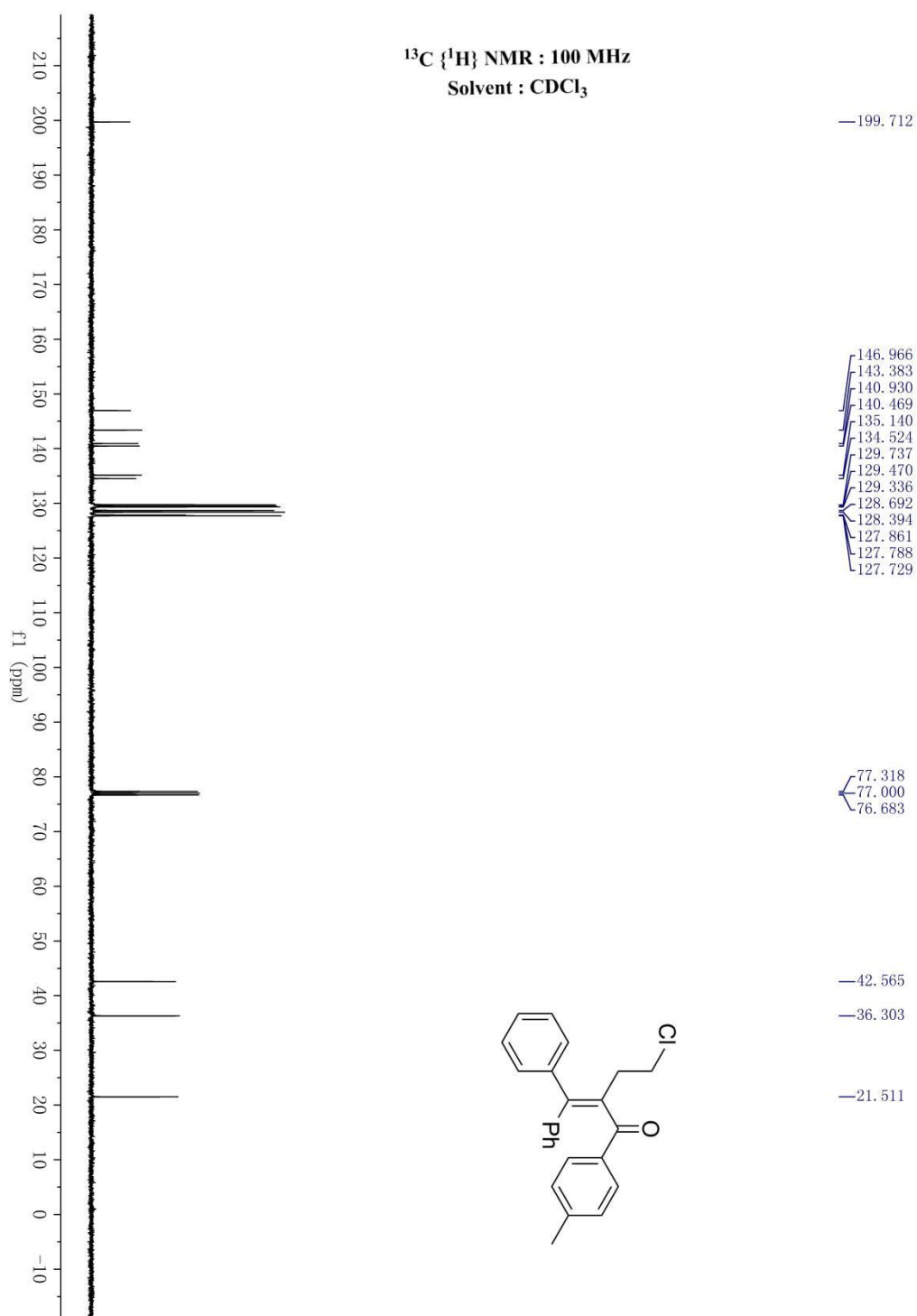




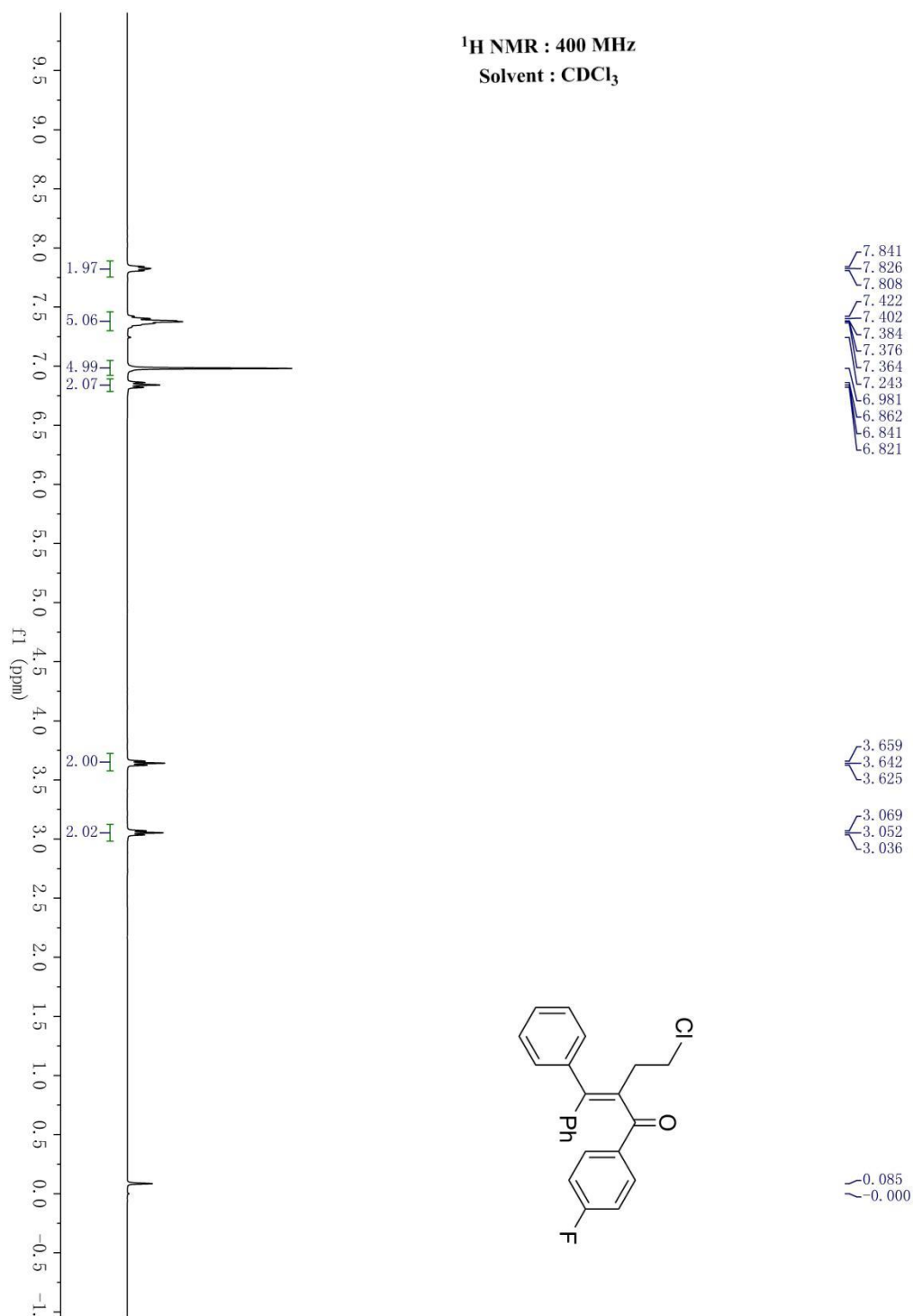


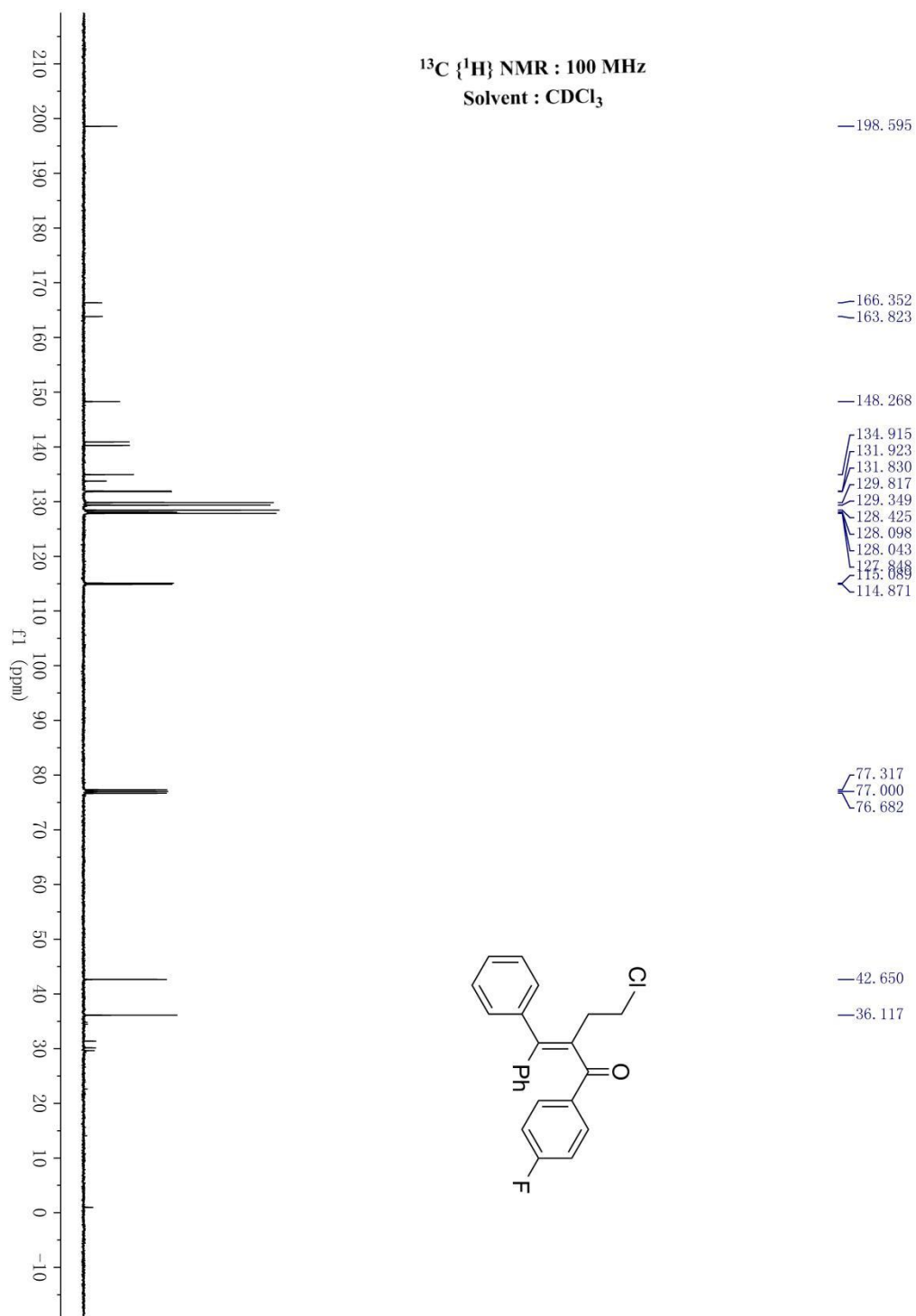
# 4-chloro-2-(diphenylmethylene)-1-(p-tolyl)butan-1-one (3ac)

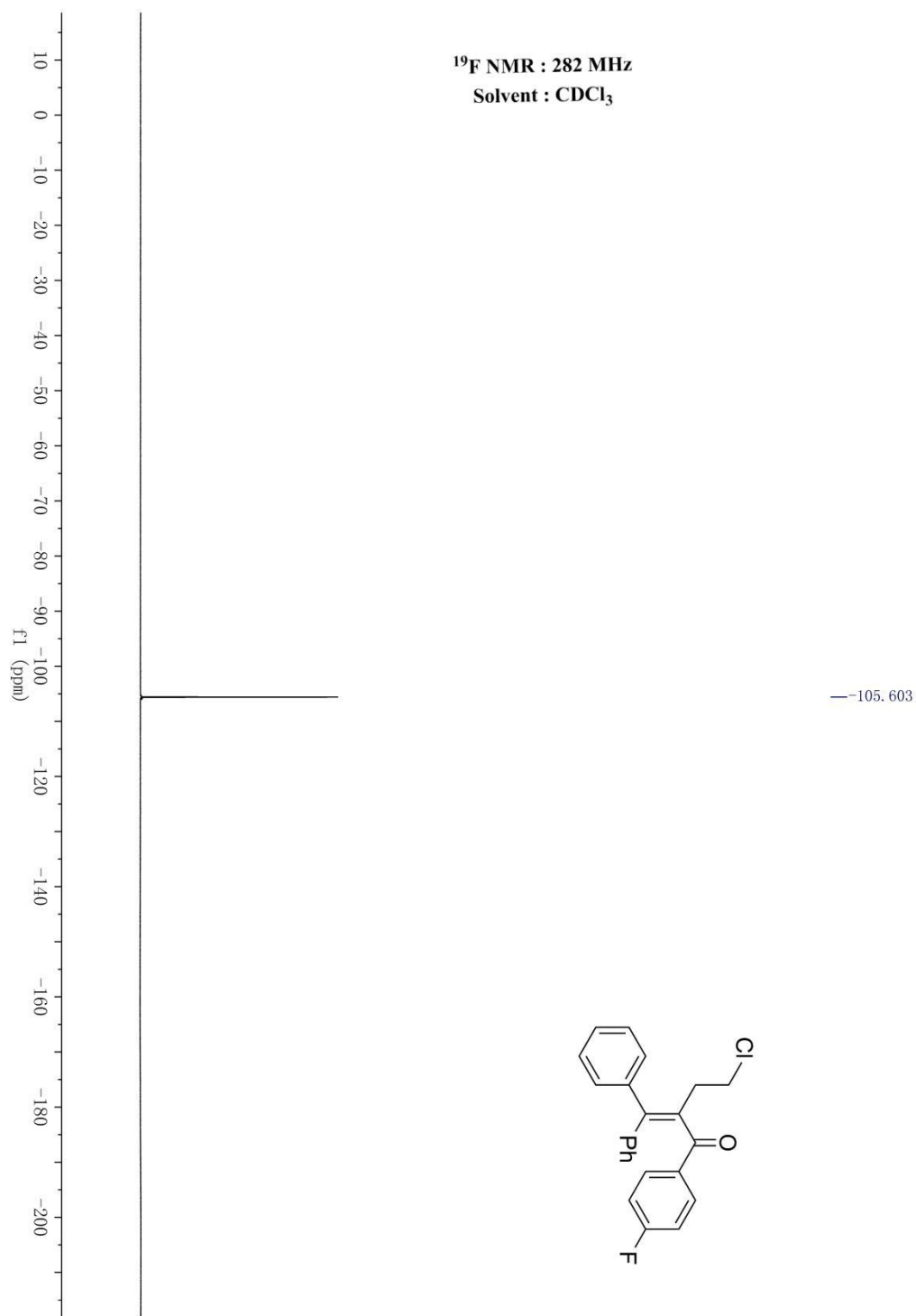




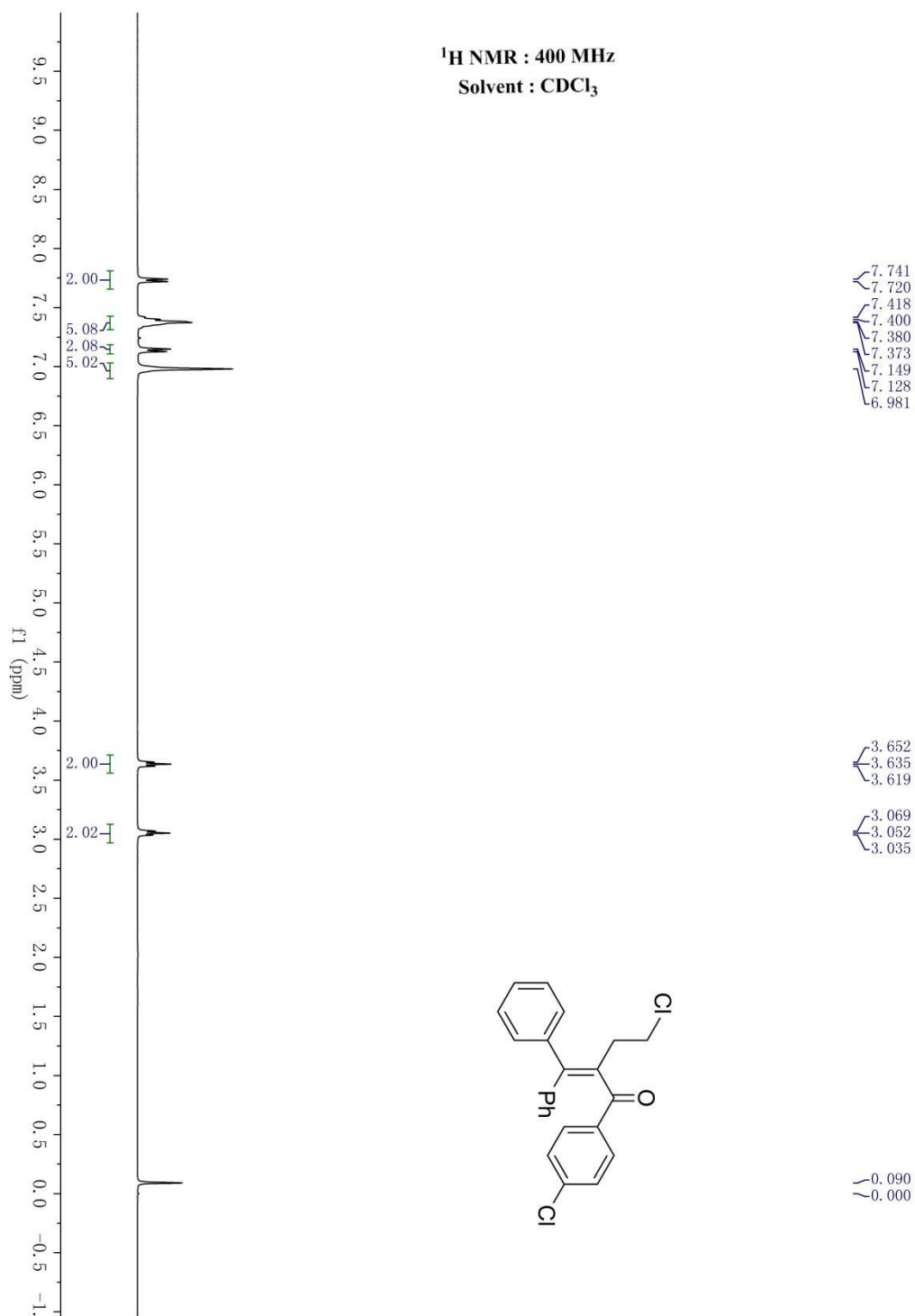
4-chloro-2-(diphenylmethylene)-1-(4-fluorophenyl)butan-1-one (3ad)



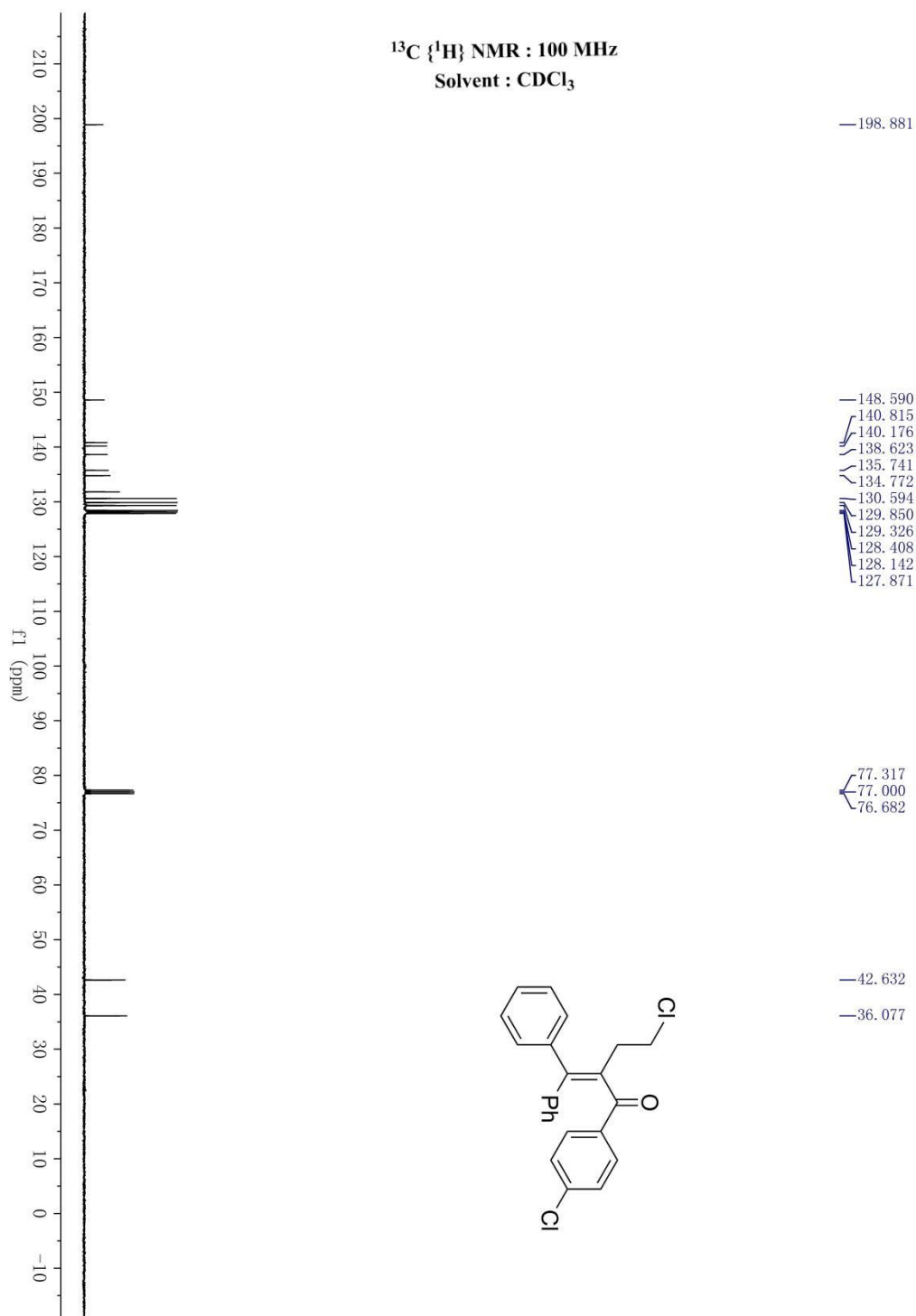




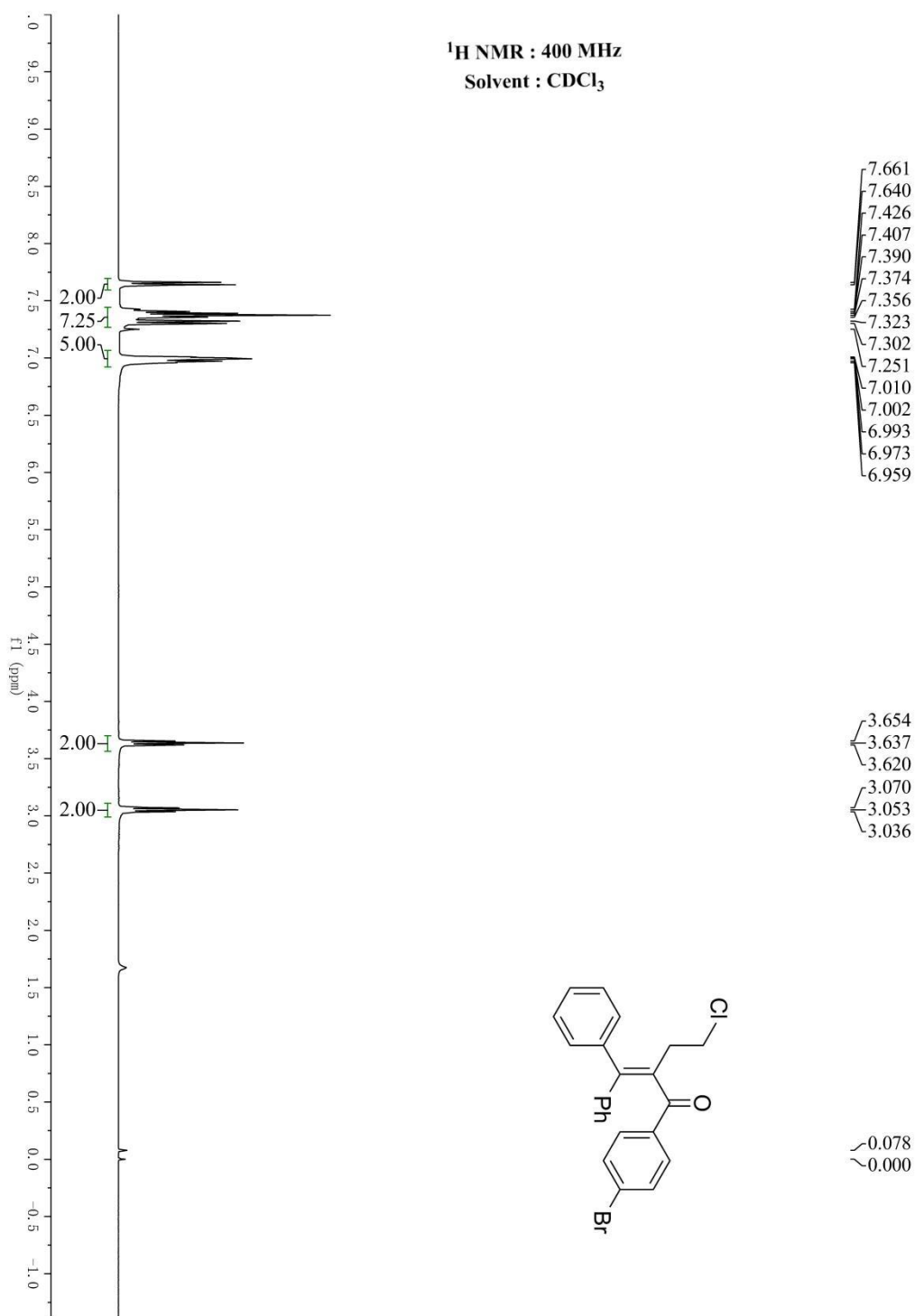
**4-chloro-1-(4-chlorophenyl)-2-(diphenylmethylene)butan-1-one (3ae)**

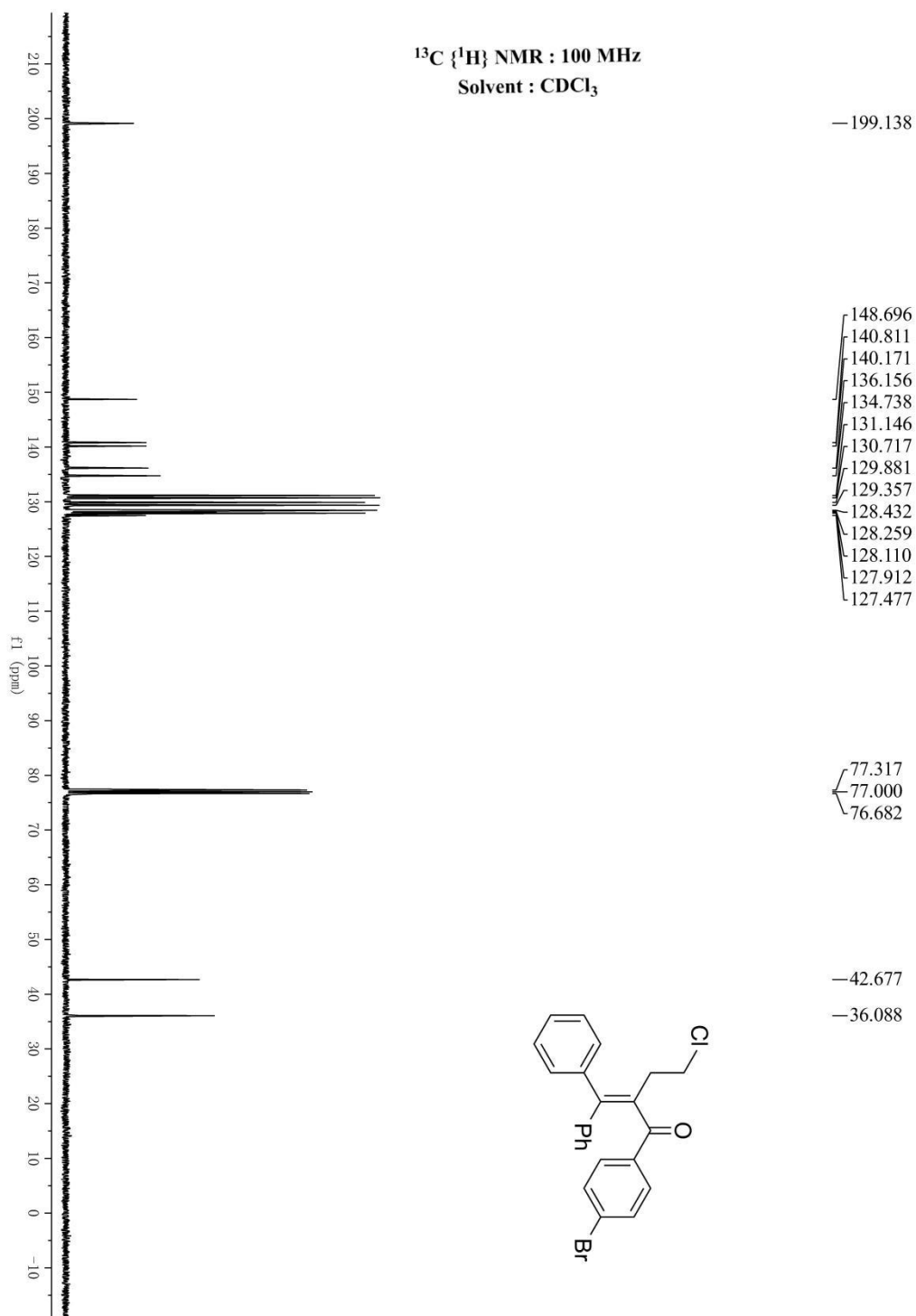




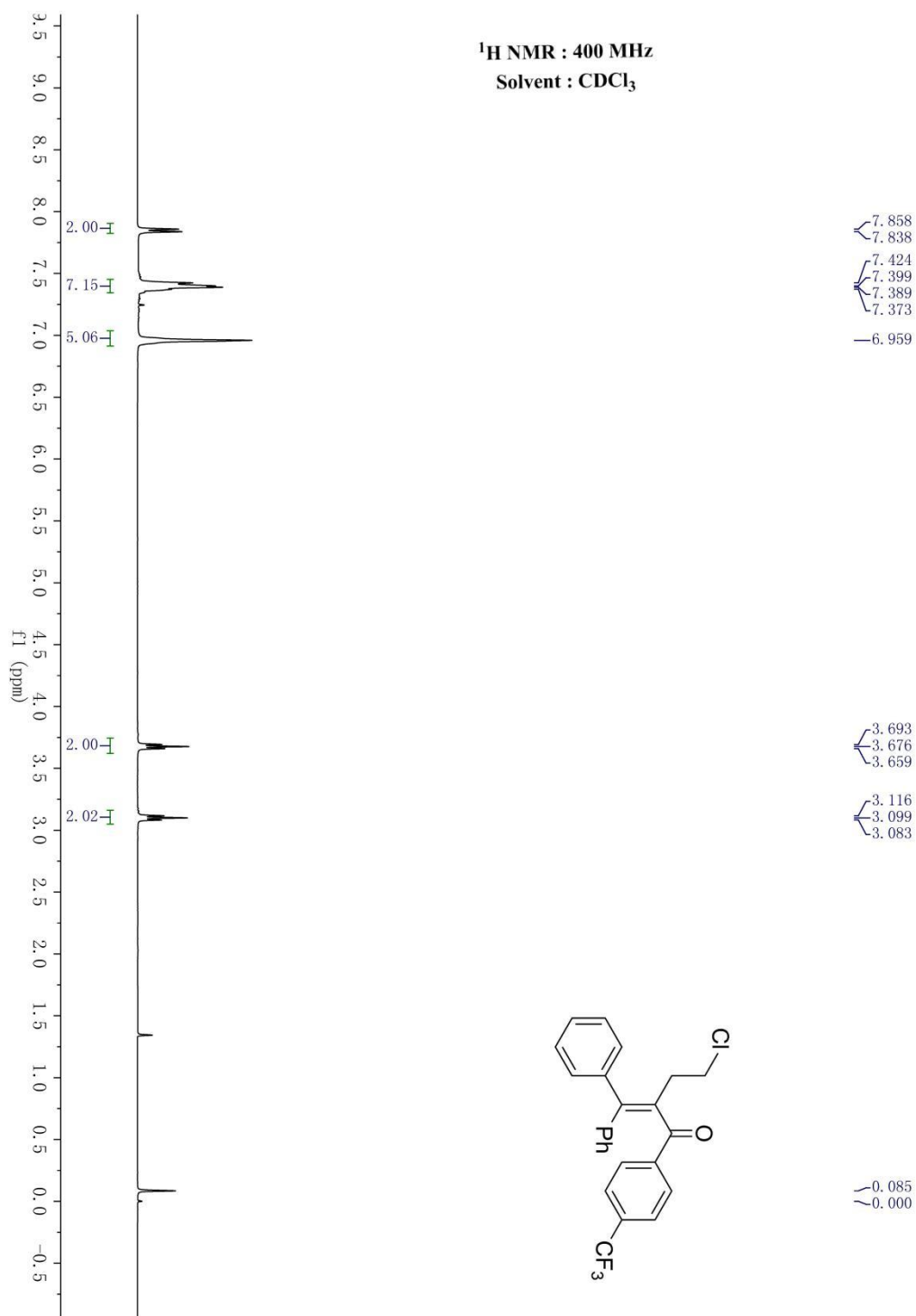


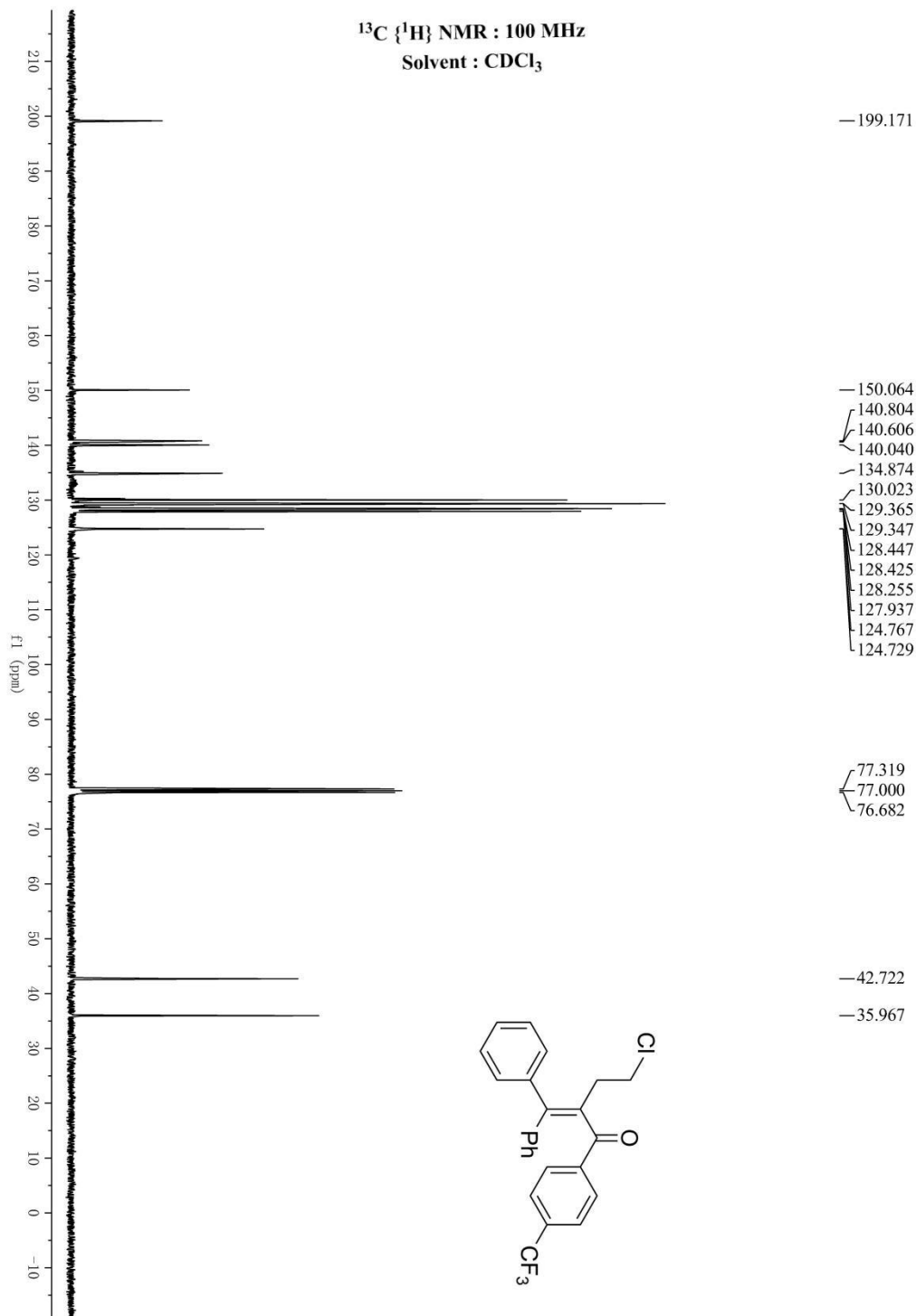
1-(4-bromophenyl)-4-chloro-2-(diphenylmethylene)butan-1-one (3af)

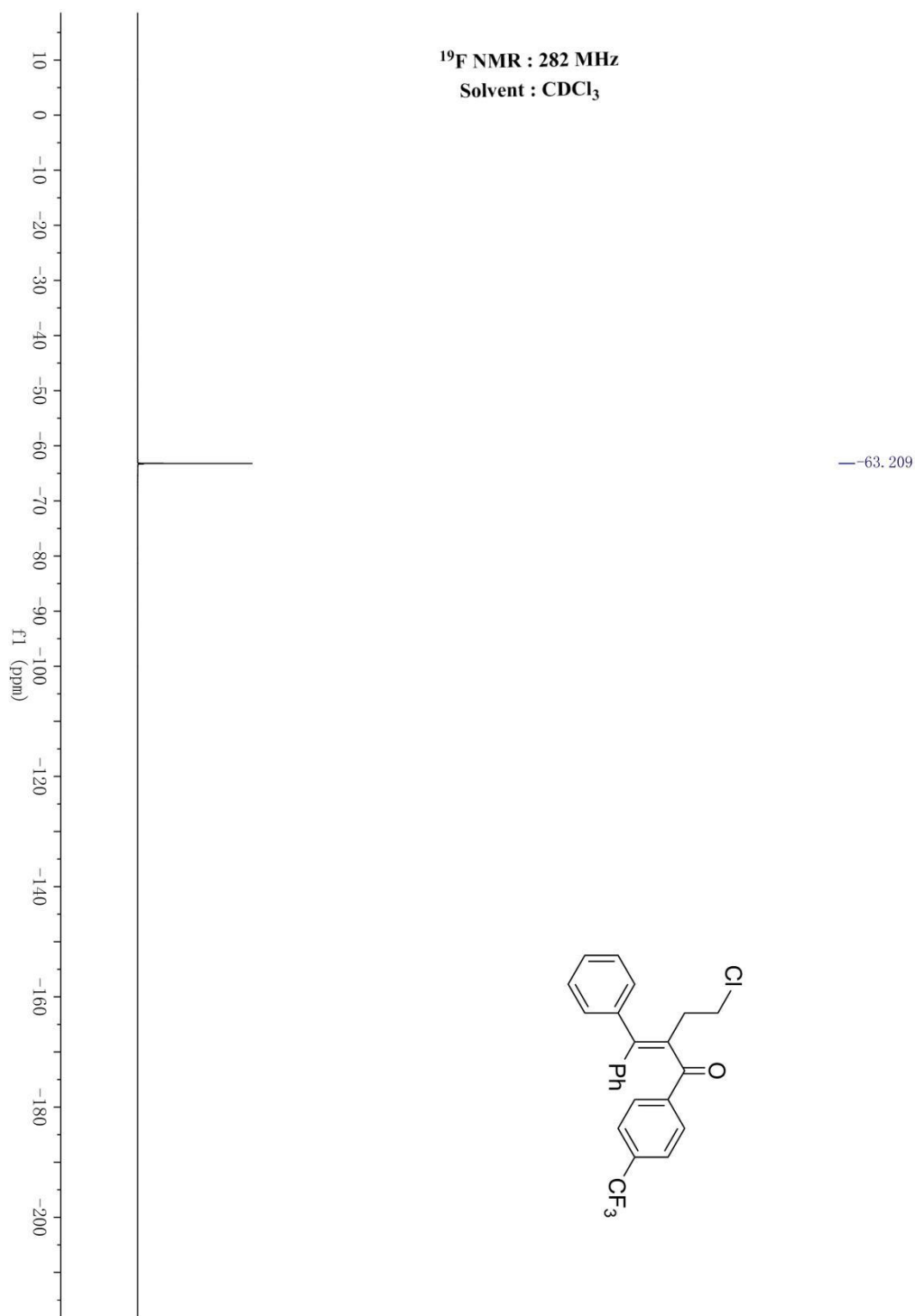




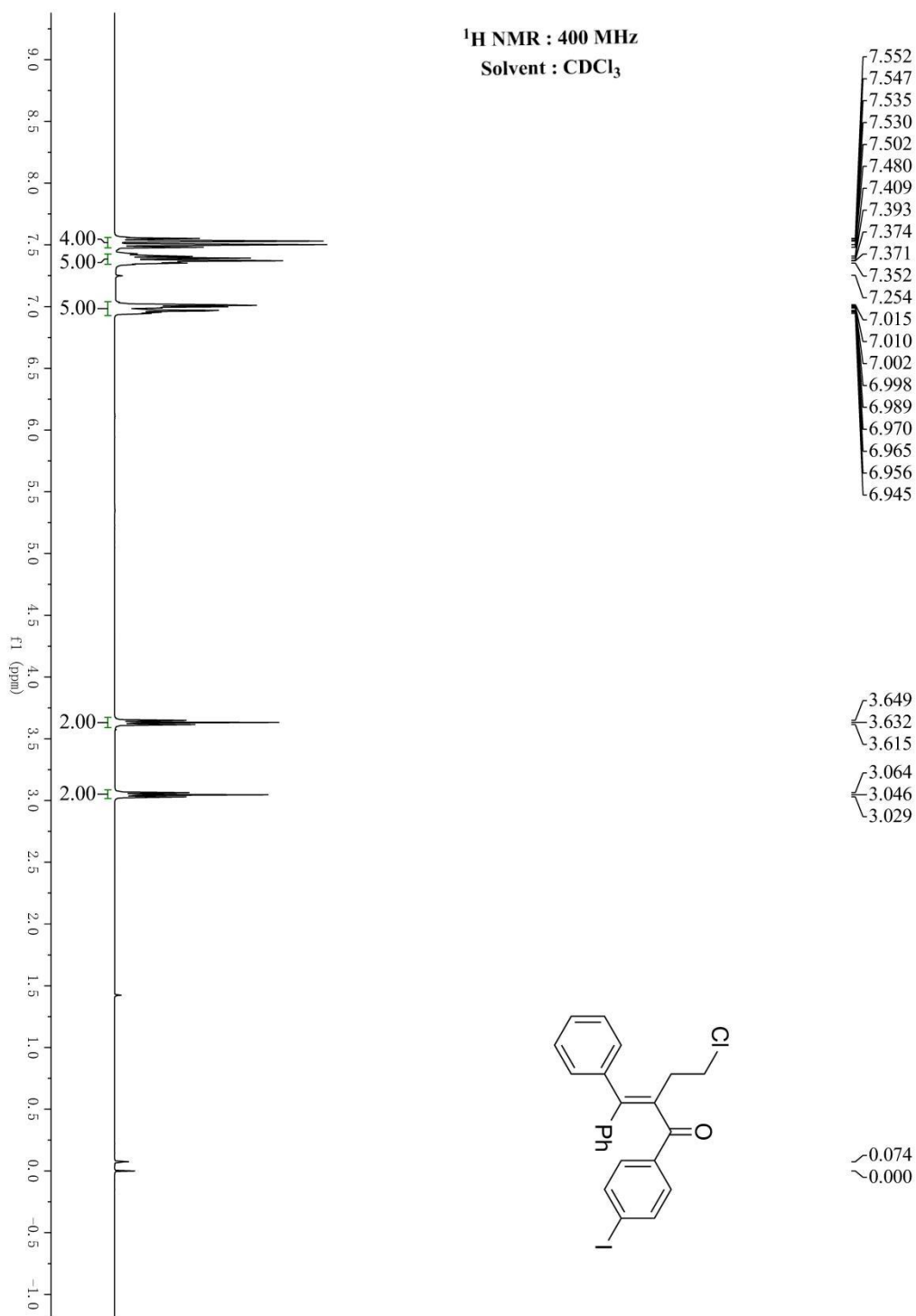
4-chloro-2-(diphenylmethylene)-1-(4-(trifluoromethyl)phenyl)butan-1-one (3ag)

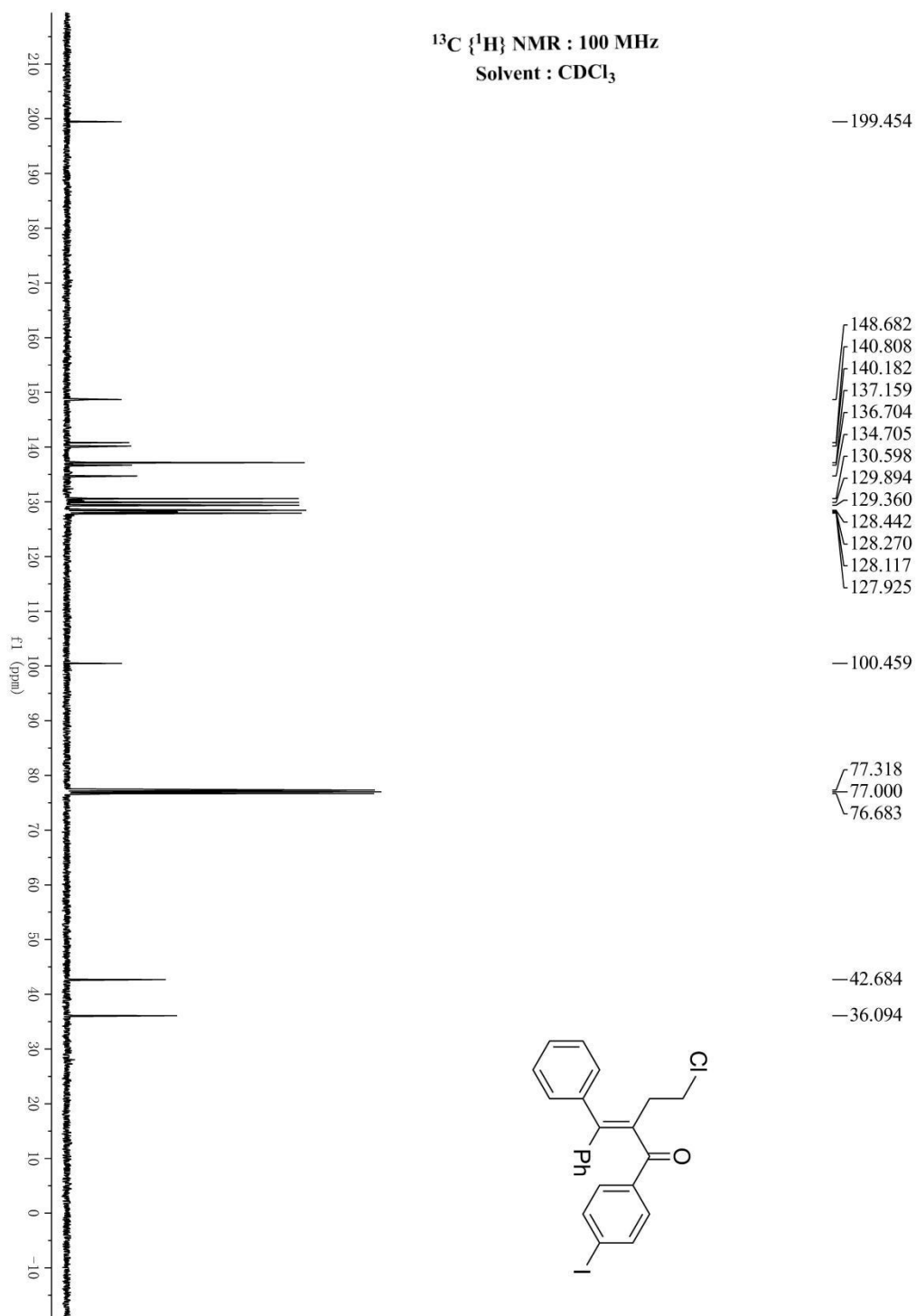






**4-chloro-2-(diphenylmethylene)-1-(4-iodophenyl)butan-1-one (3ah)**

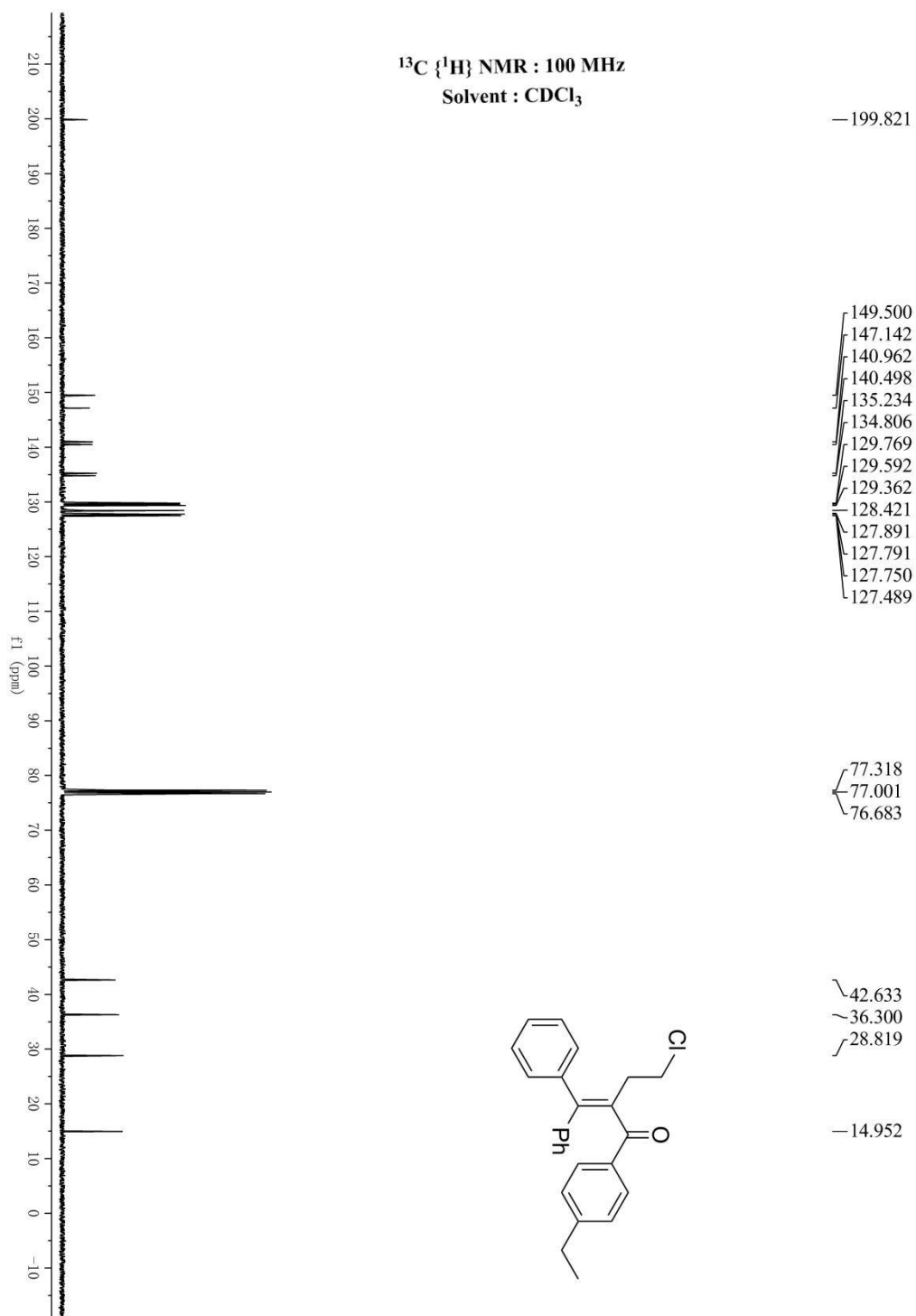




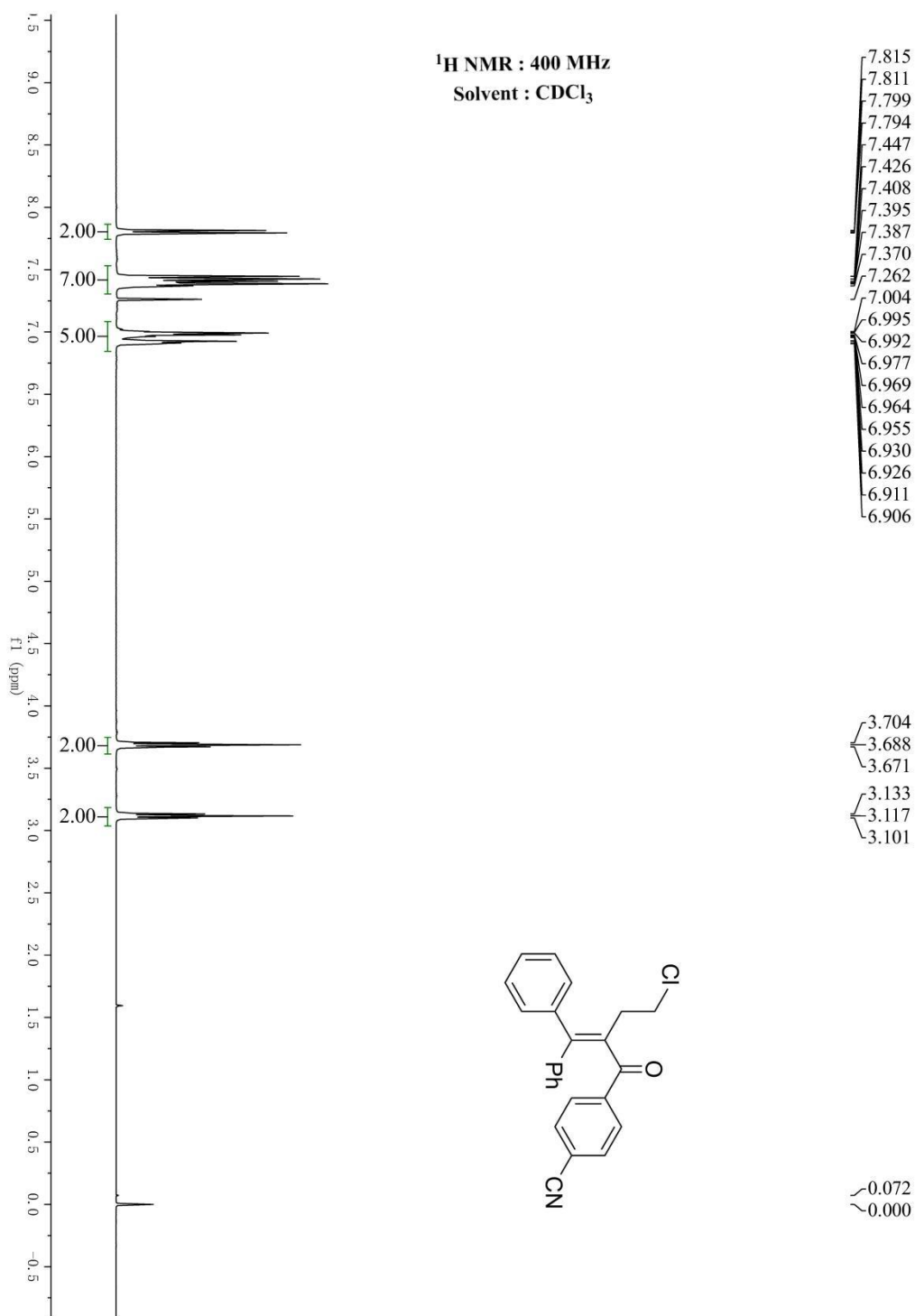
4-chloro-2-(diphenylmethylene)-1-(4-ethylphenyl)butan-1-one (3ai)

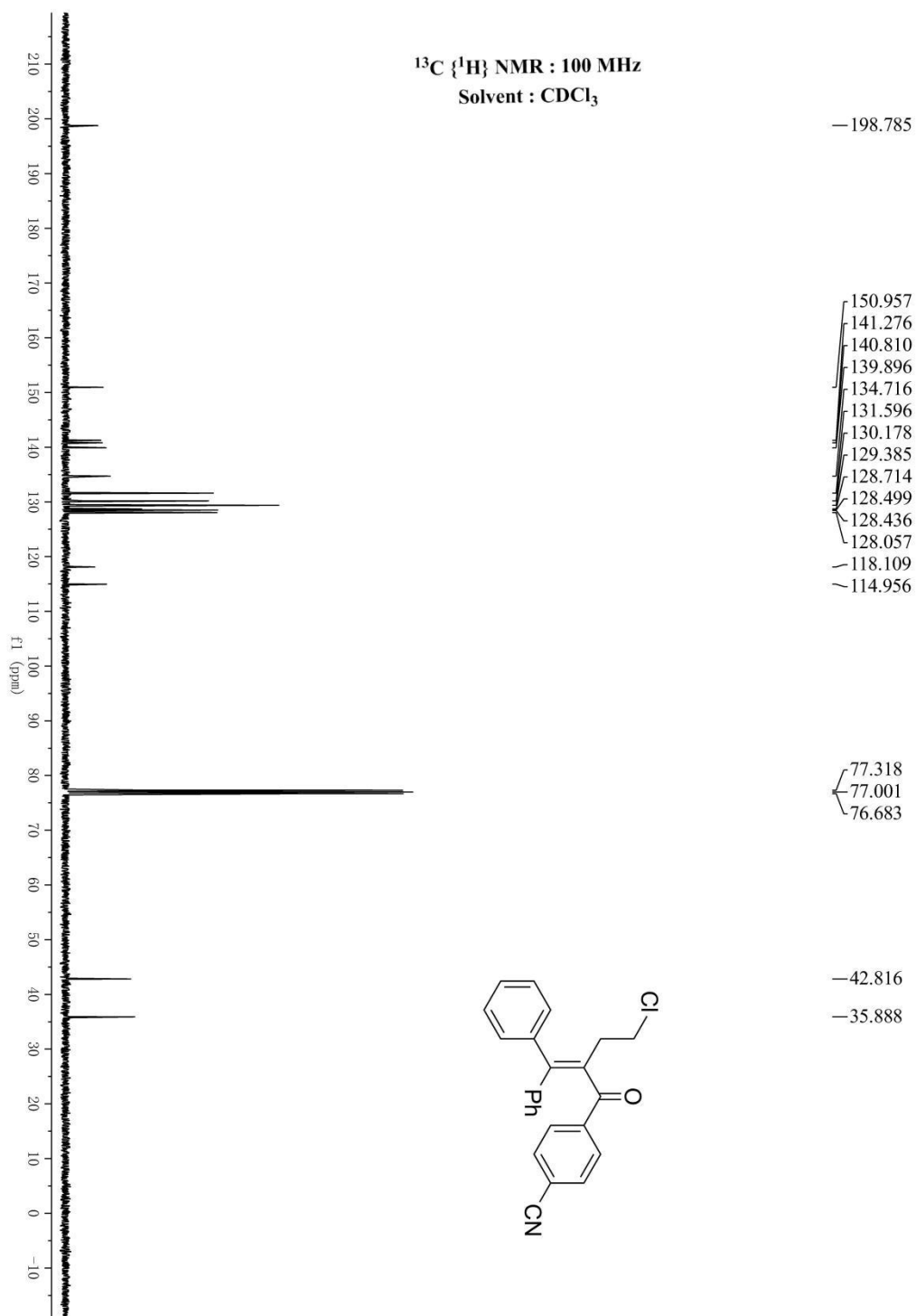




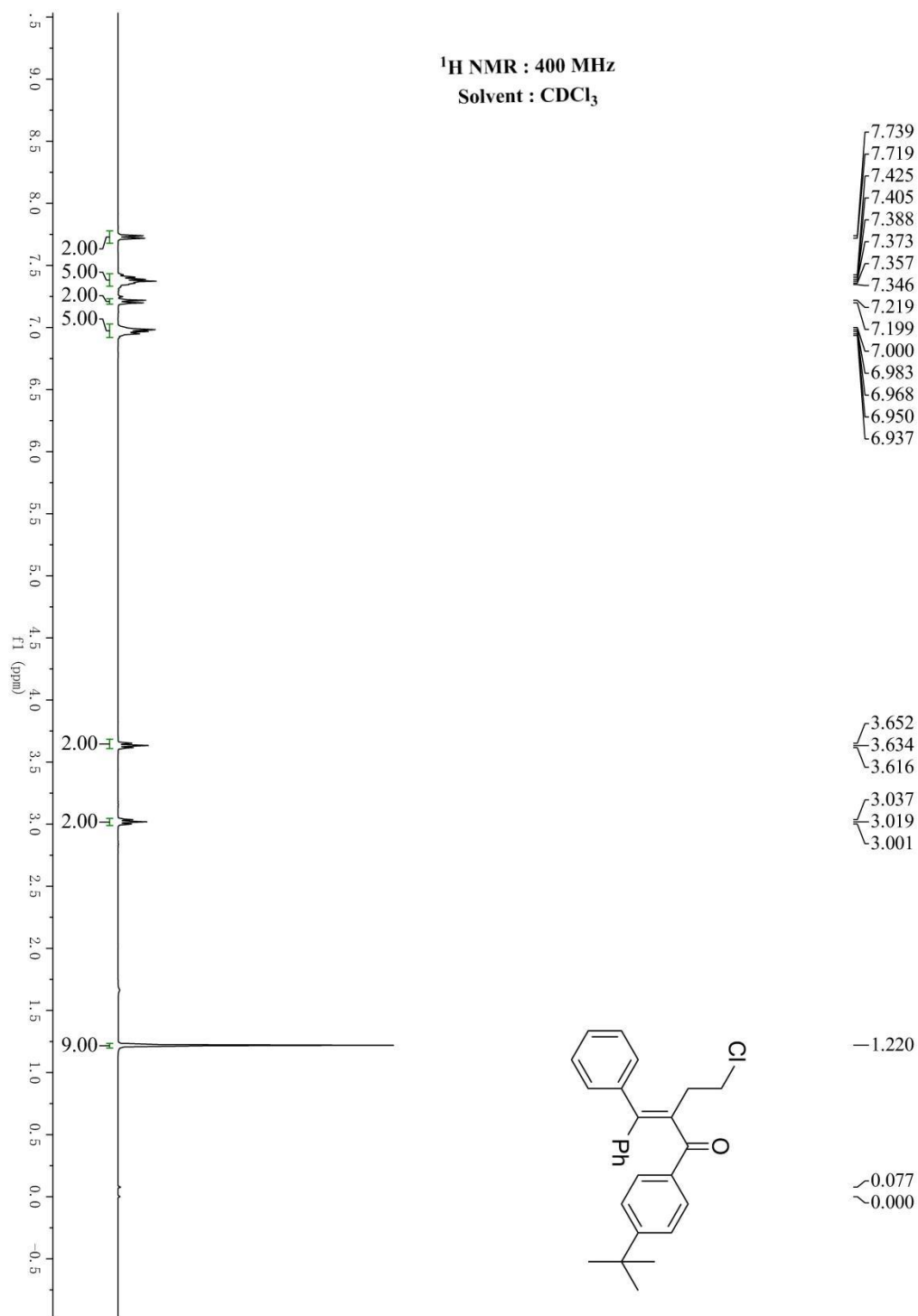


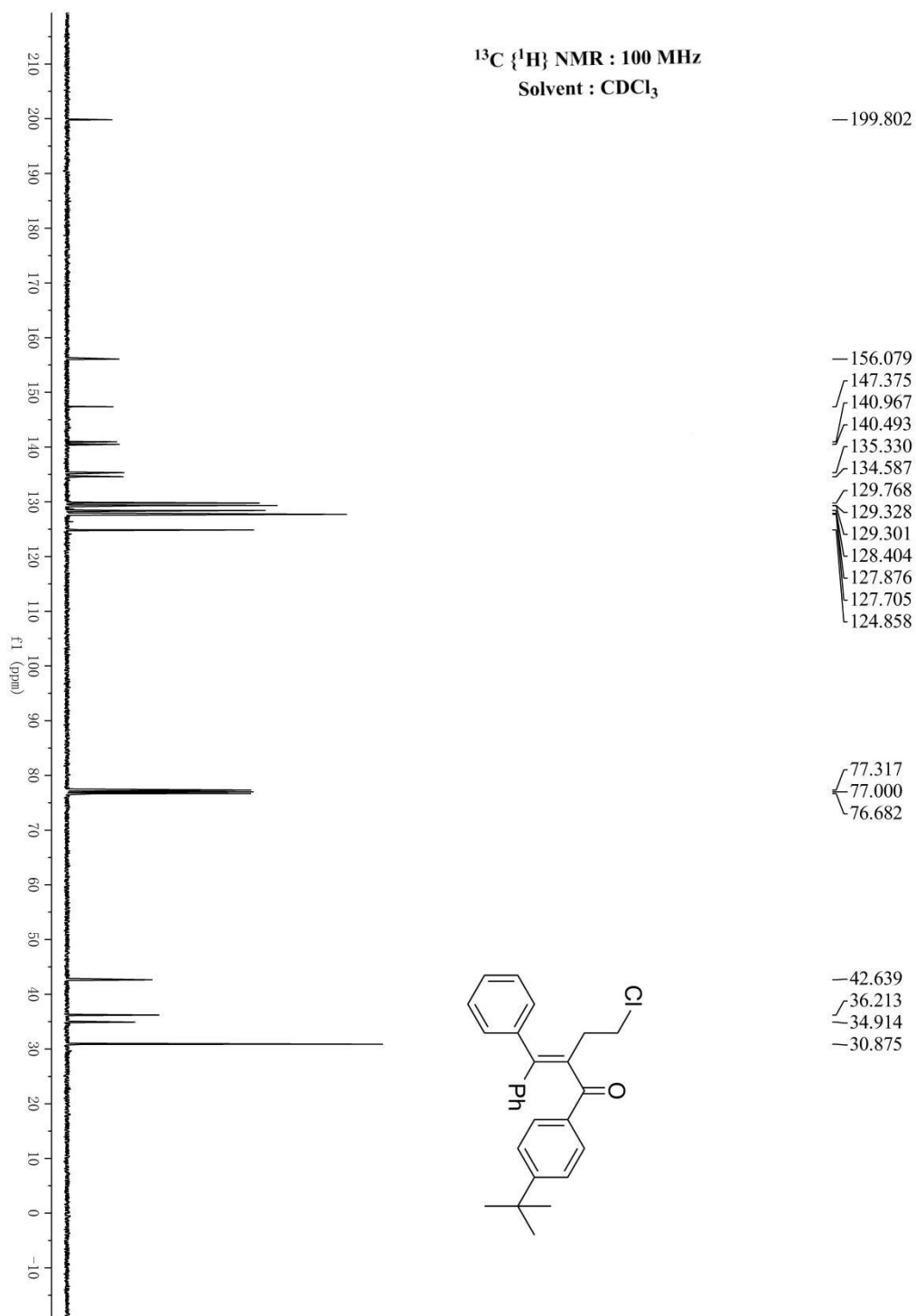
4-(4-chloro-2-(diphenylmethylene)butanoyl)benzonitrile (3aj)



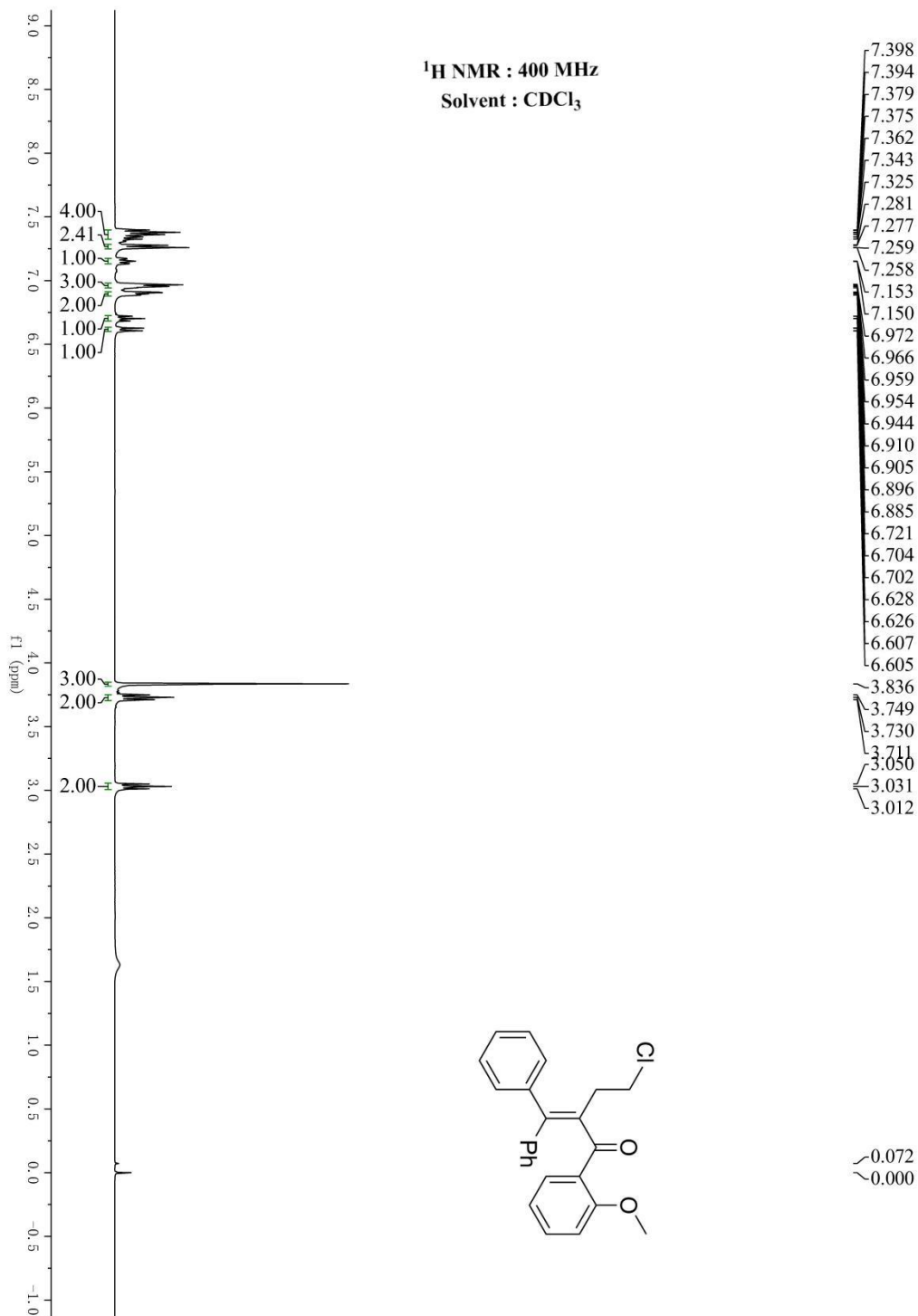


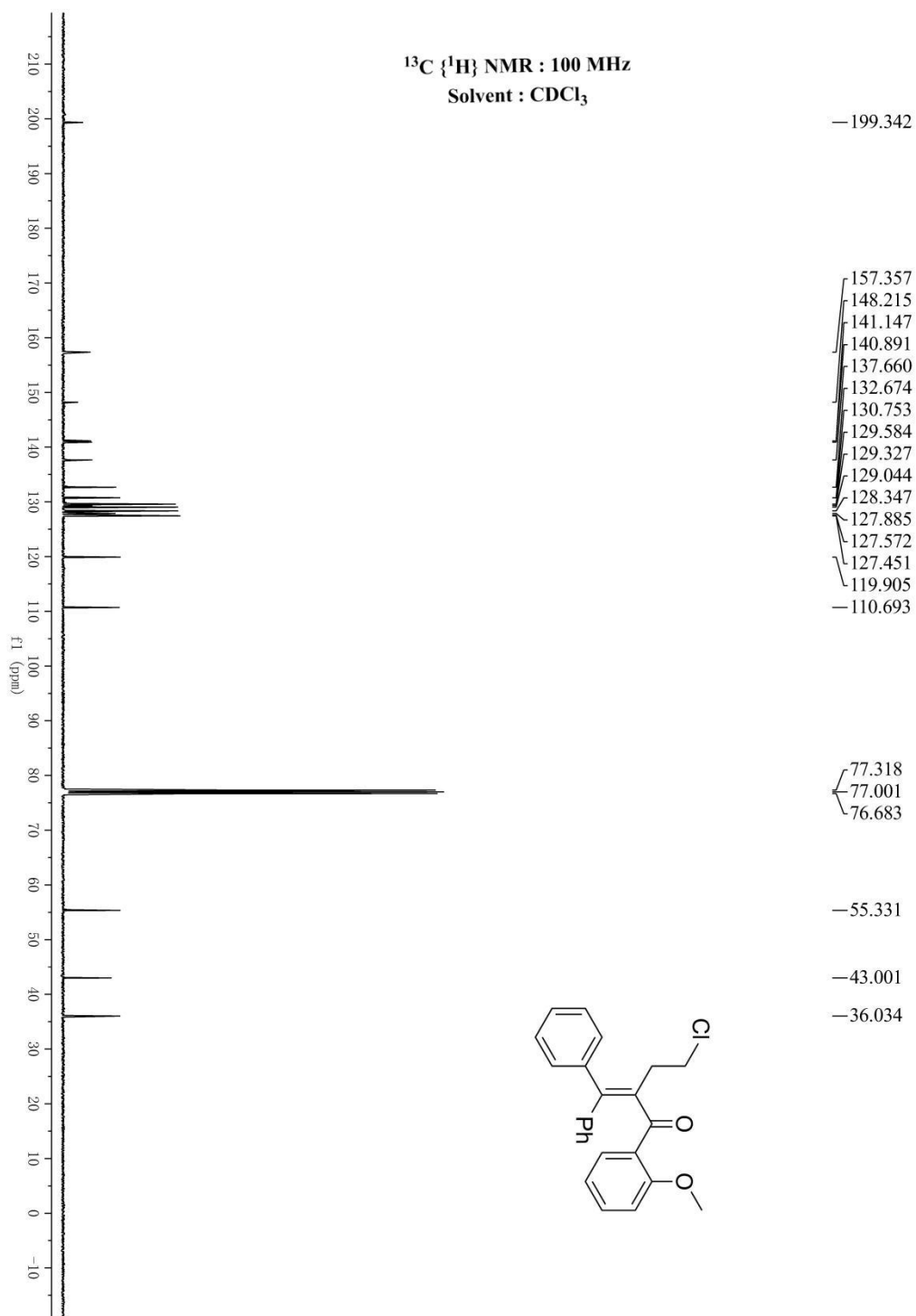
**1-(4-(tert-butyl)phenyl)-4-chloro-2-(diphenylmethylene)butan-1-one (3ak)**





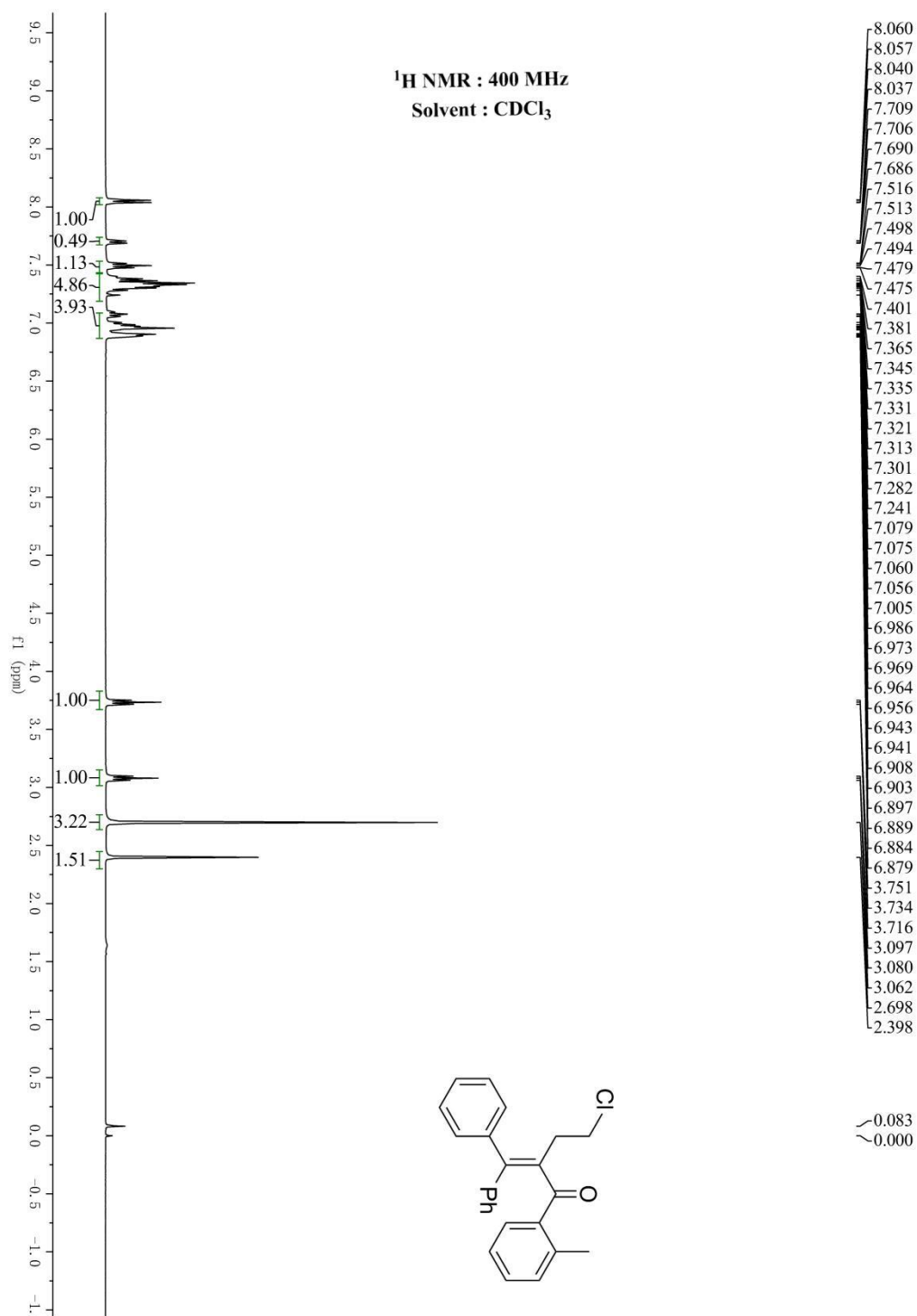
chloro-2-(diphenylmethylene)-1-(2-methoxyphenyl)butan-1-one (3aI)

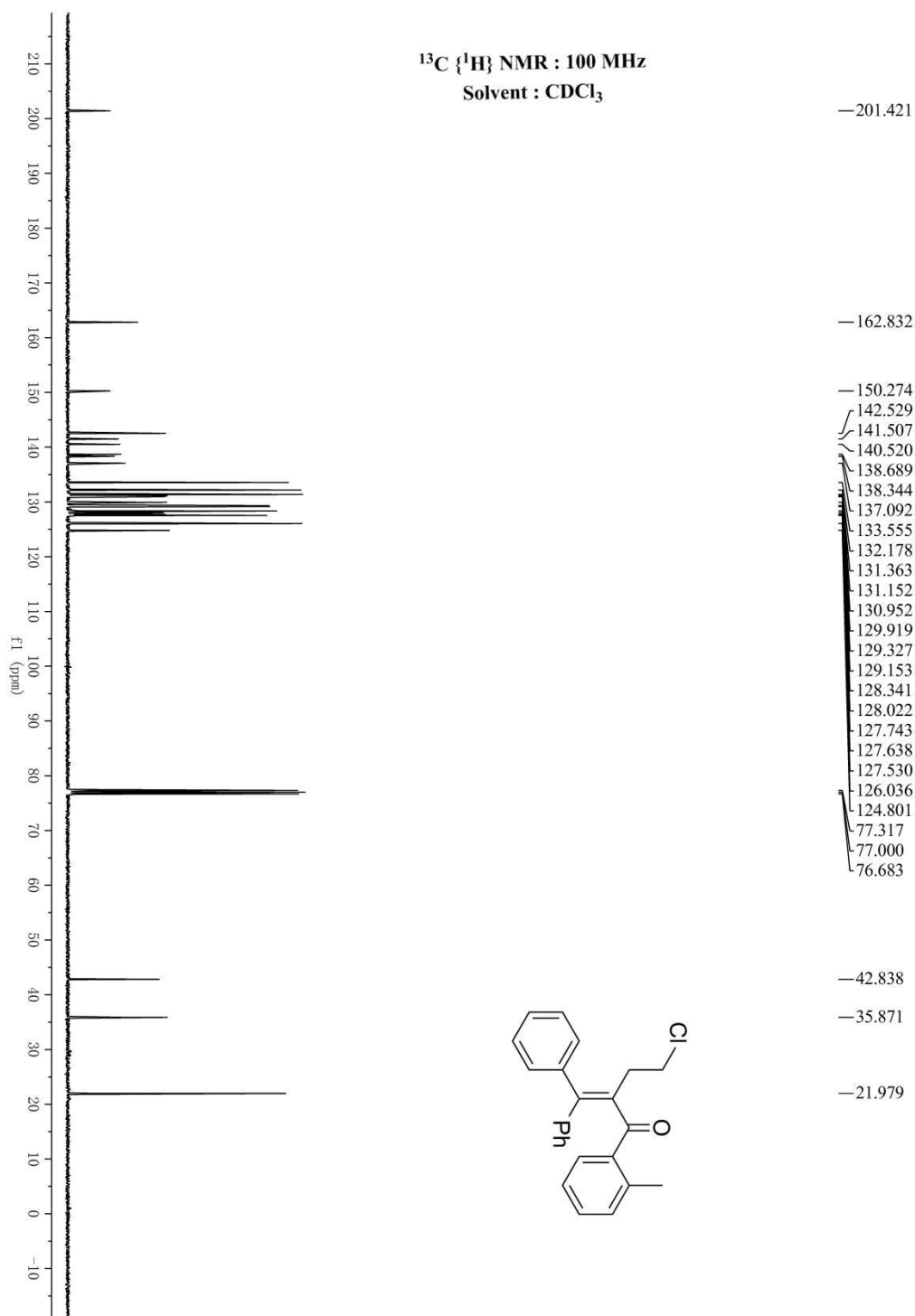




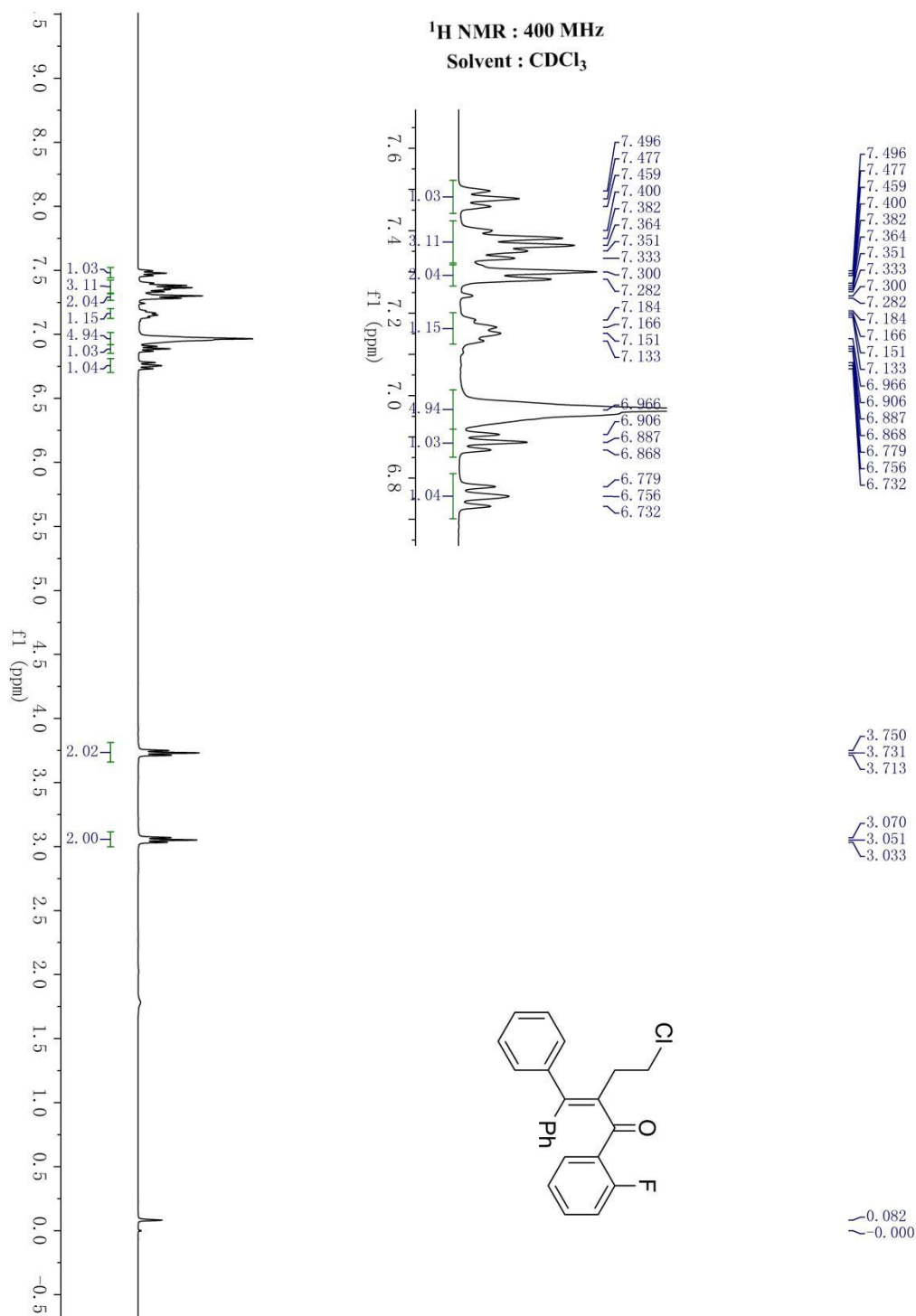


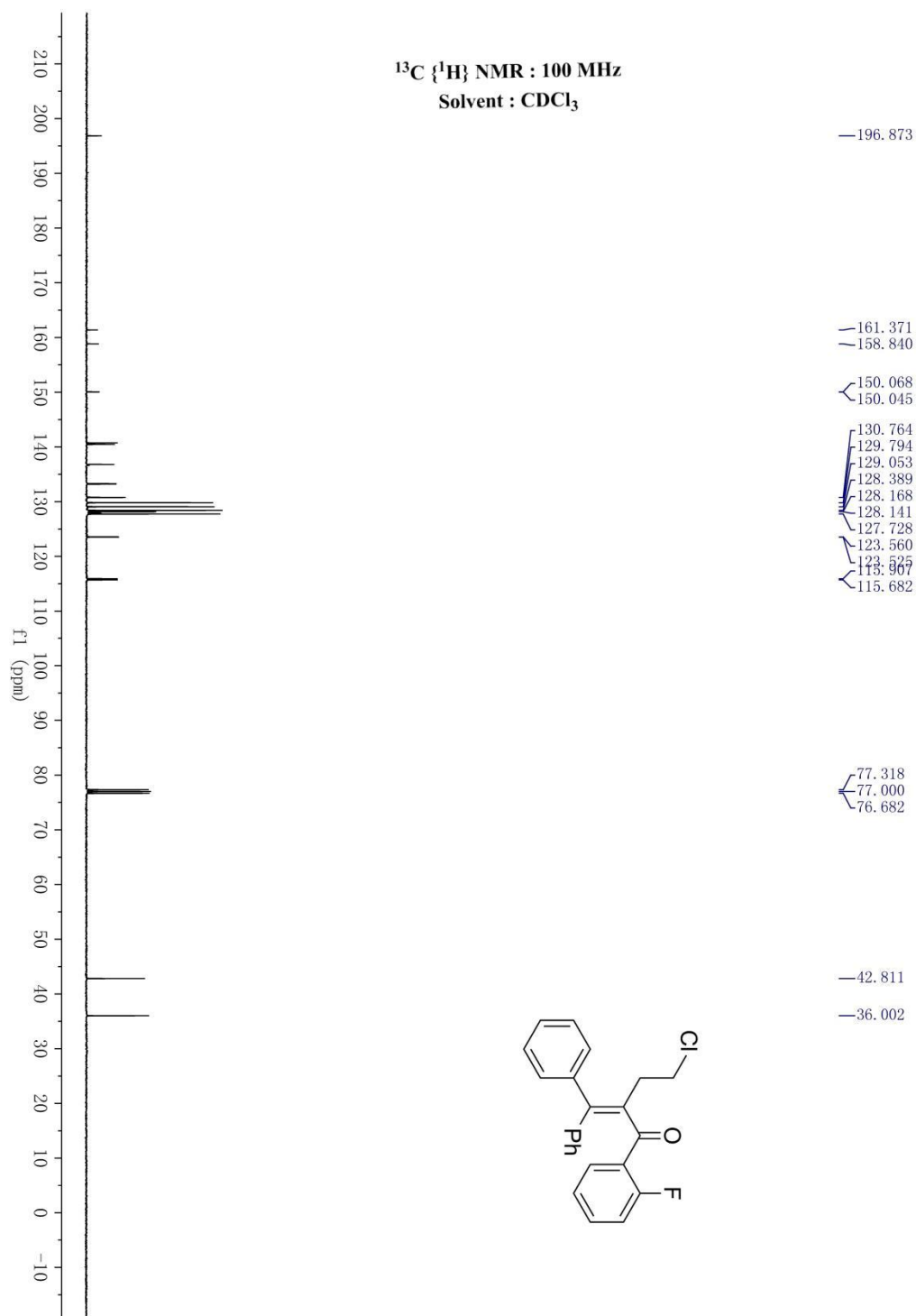
4-chloro-2-(diphenylmethylene)-1-(o-tolyl)butan-1-one(3am)

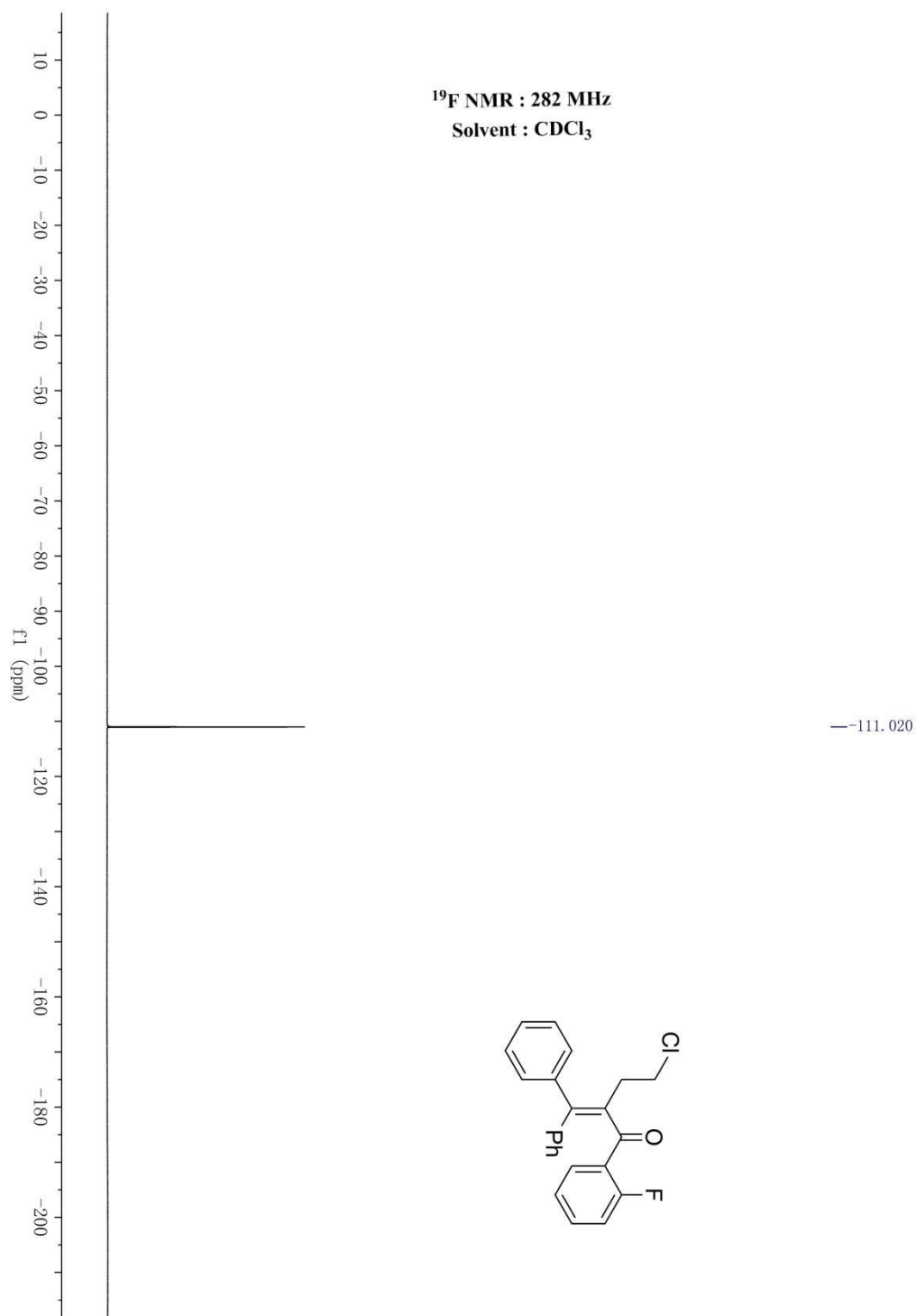




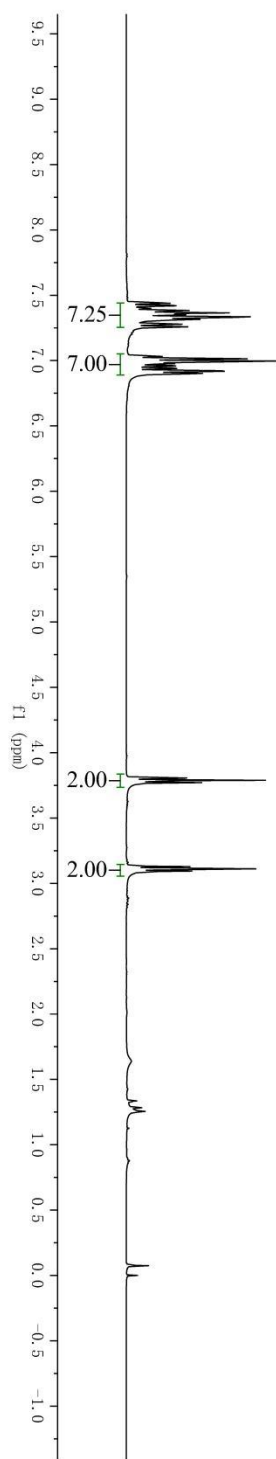
**4-Chloro-2-((2-fluorophenyl)(phenyl)methylene)-1-phenylbutan-1-one(3an)**







**1-(2-bromophenyl)-4-chloro-2-(diphenylmethylene)butan-1-one (3ao)**

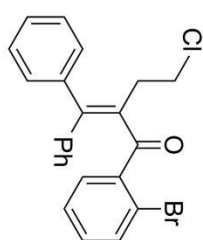


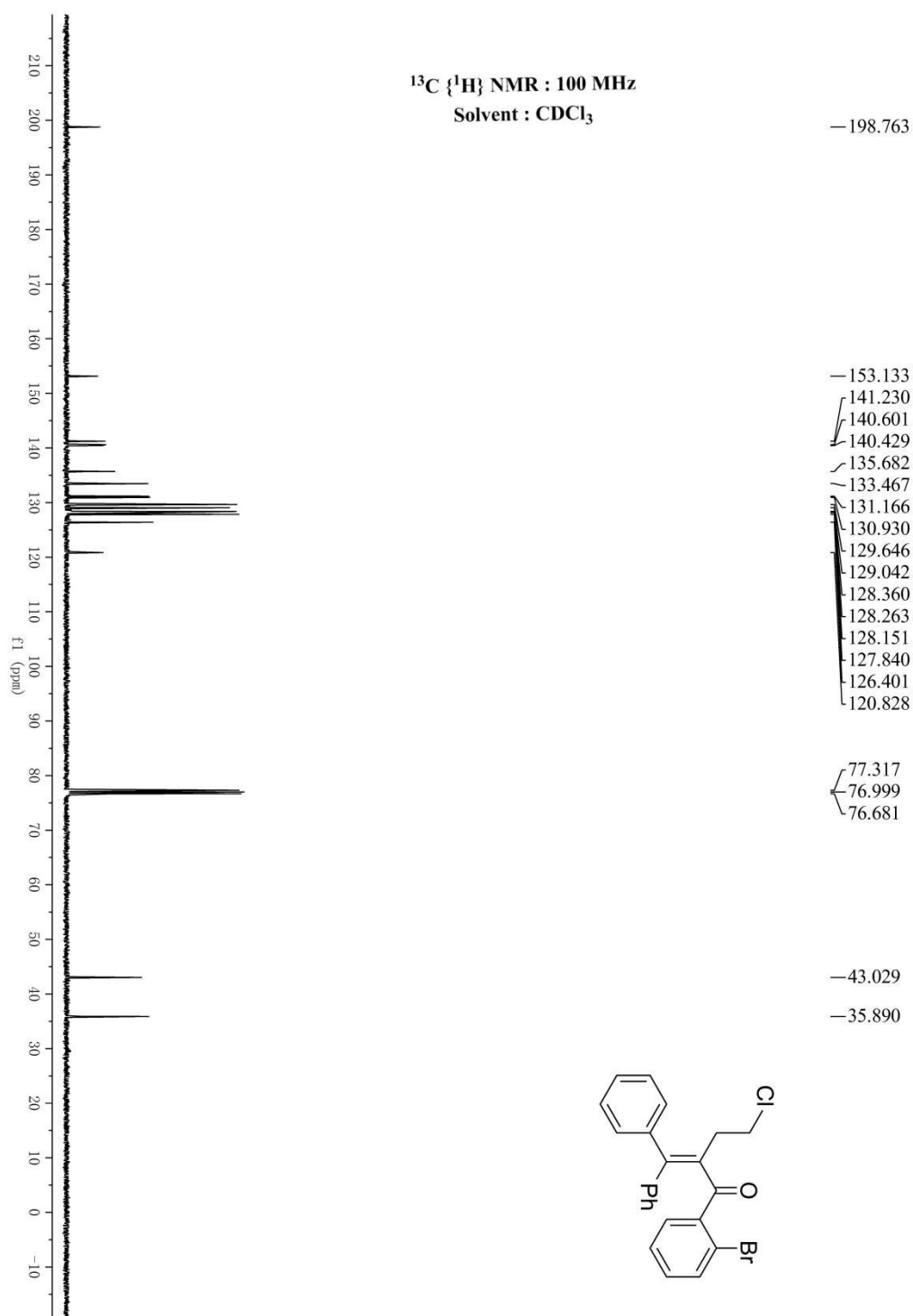
7.442  
7.438  
7.423  
7.419  
7.400  
7.384  
7.365  
7.355  
7.351  
7.335  
7.331  
7.315  
7.278  
7.258  
7.254  
7.035  
7.032  
7.014  
6.997  
6.977  
6.962  
6.958  
6.943  
6.939  
6.922  
6.918  
6.903  
6.899

3.806  
3.788  
3.771

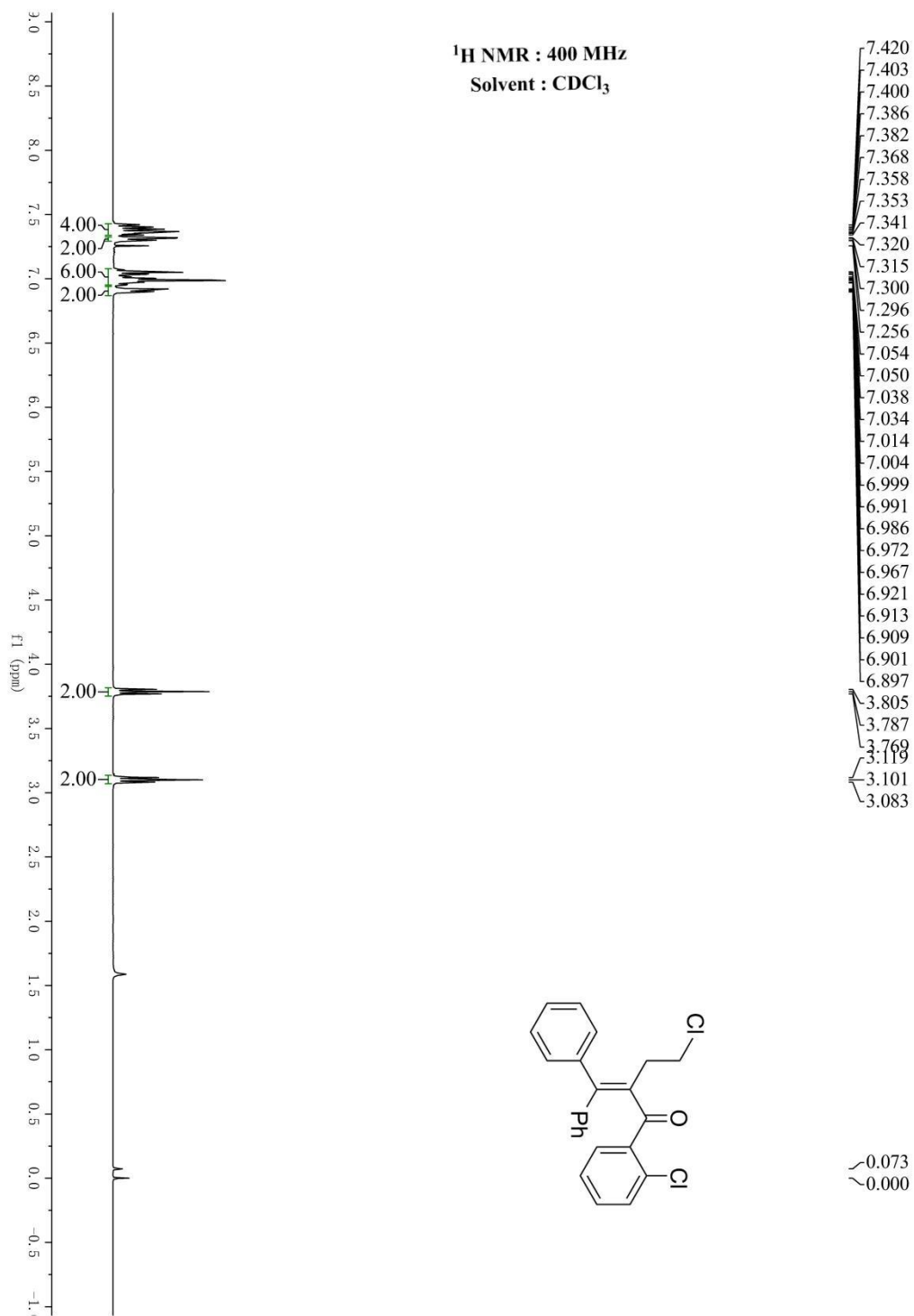
3.129  
3.111  
3.094

0.075  
0.000

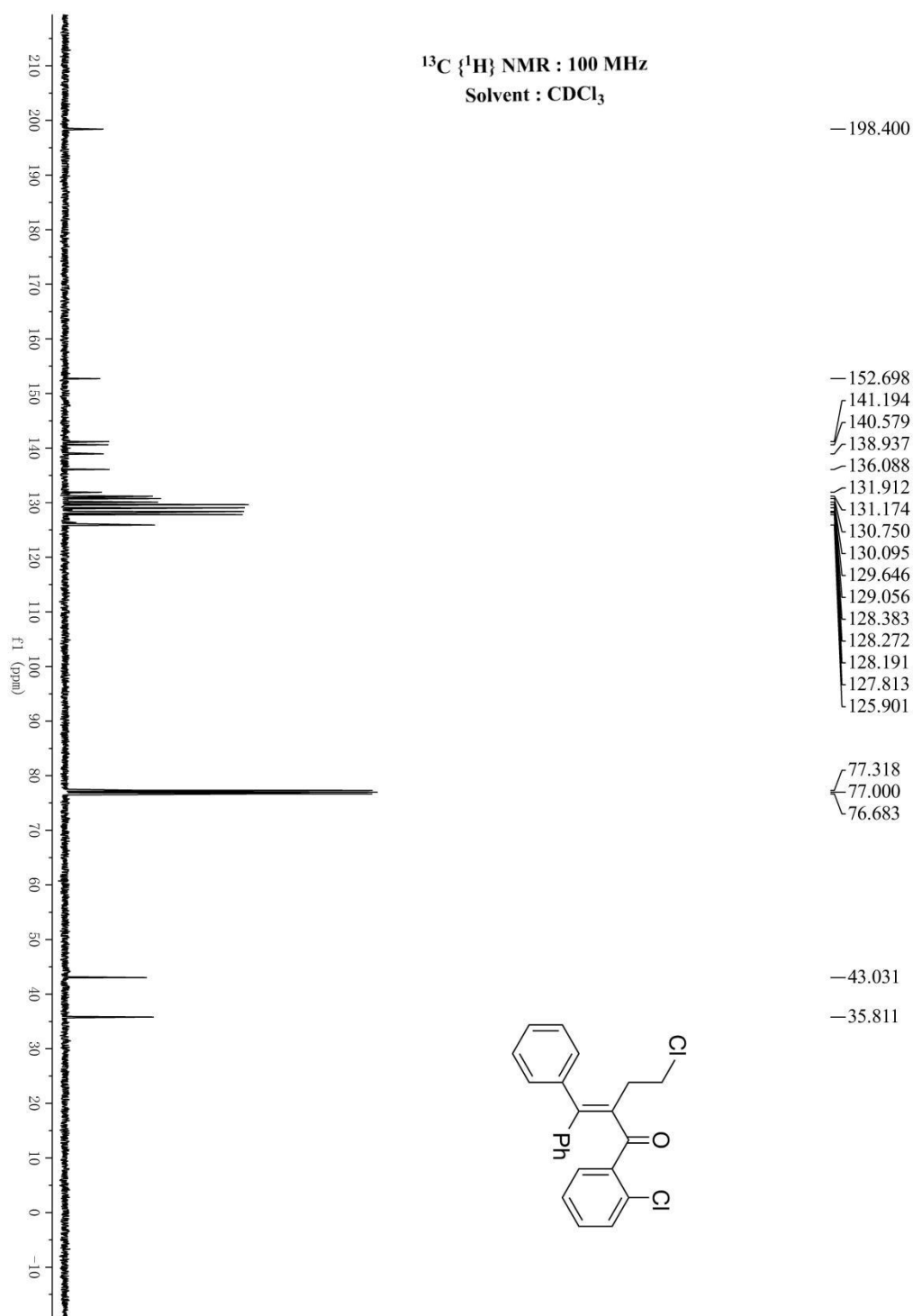




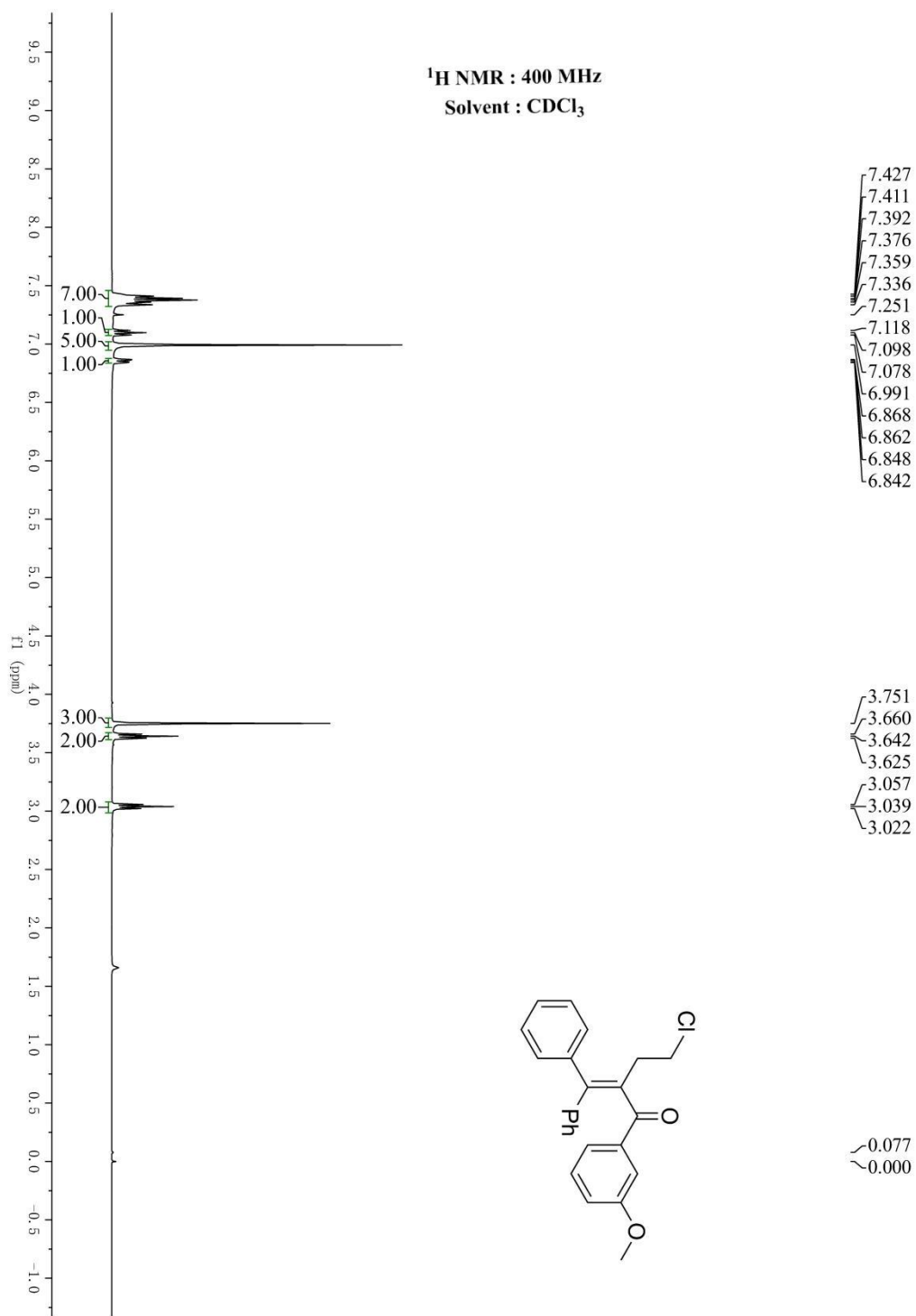
4-chloro-2-(diphenylmethylene)-1-(2-methoxyphenyl)butan-1-one (3ap)

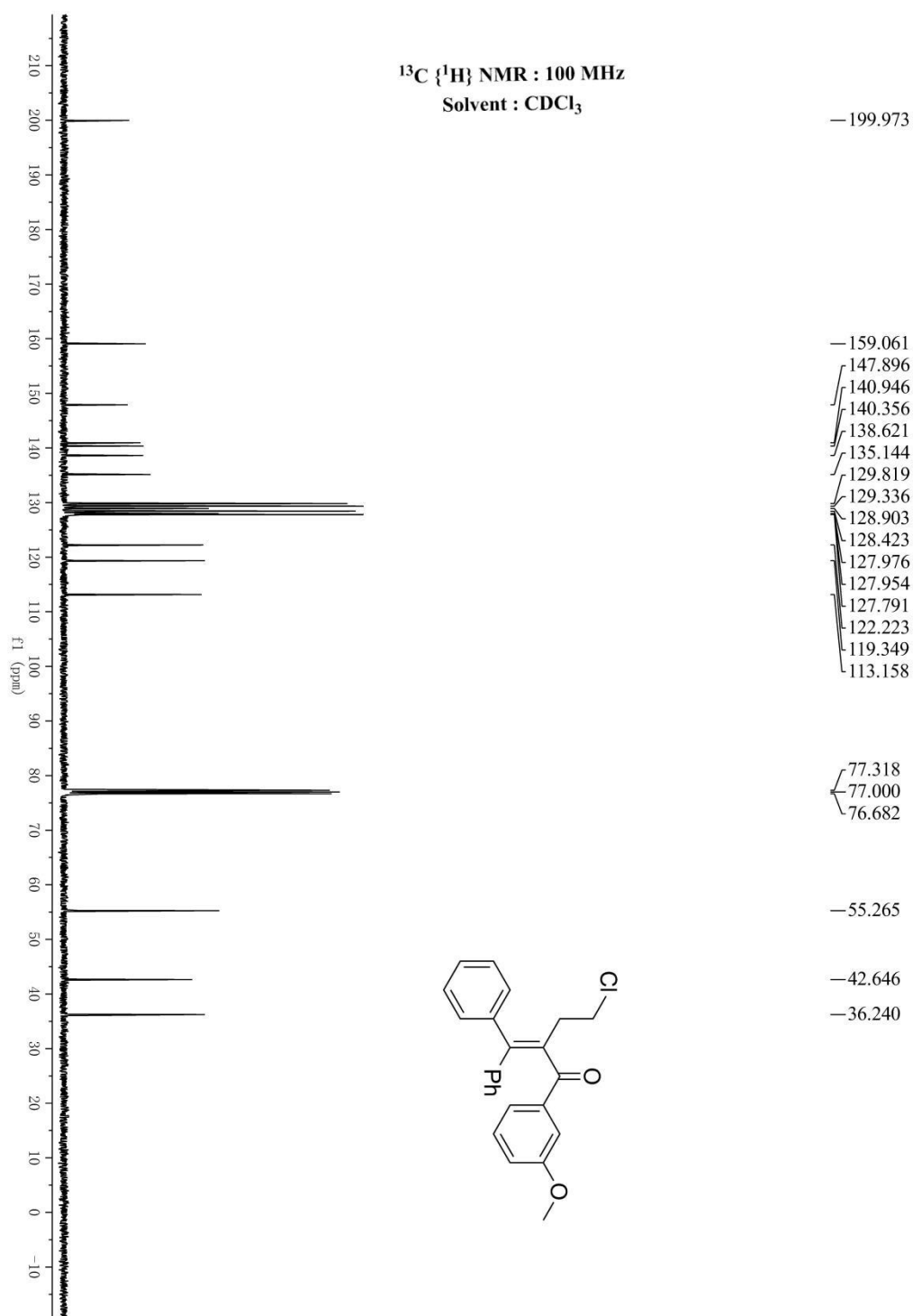




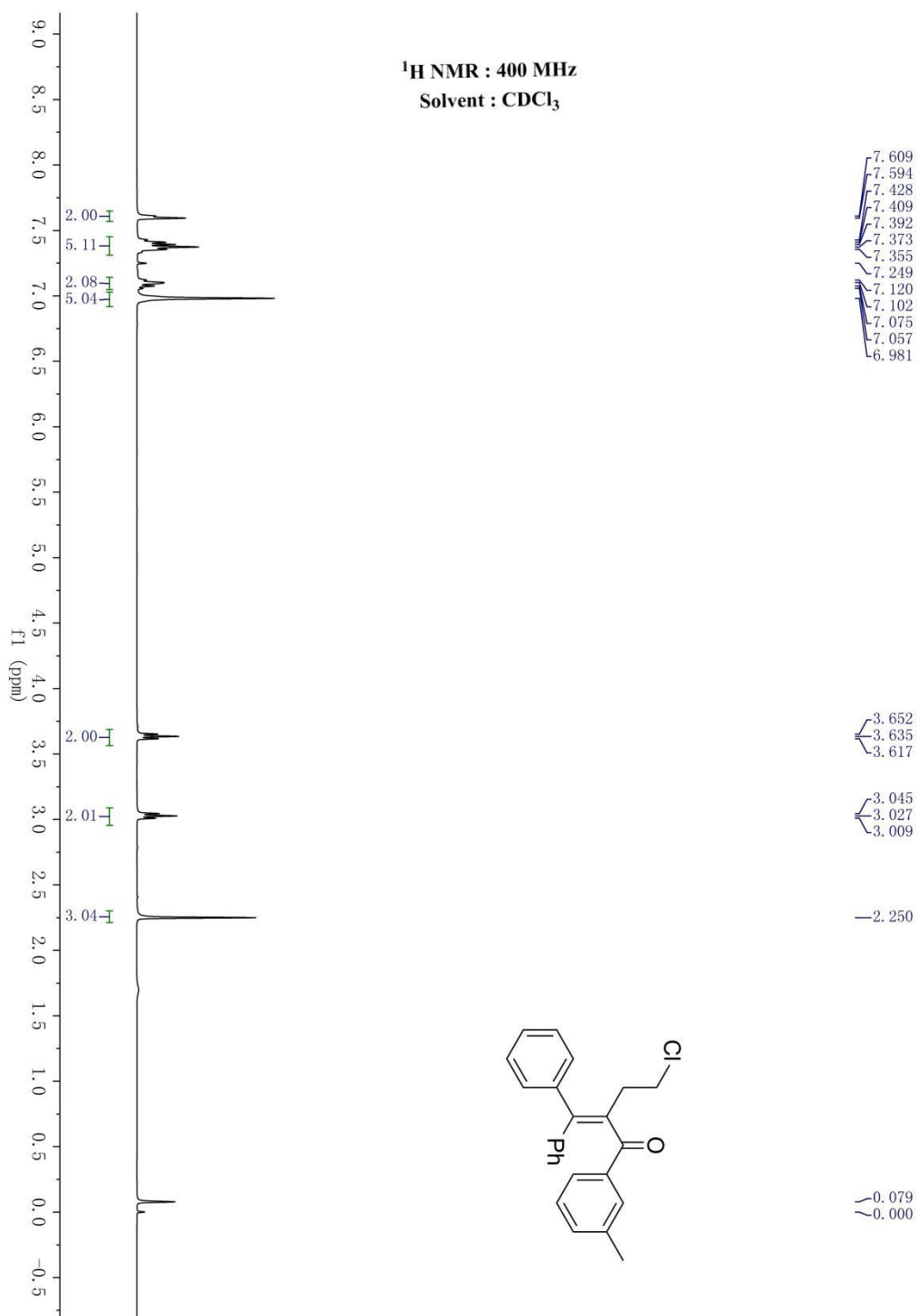


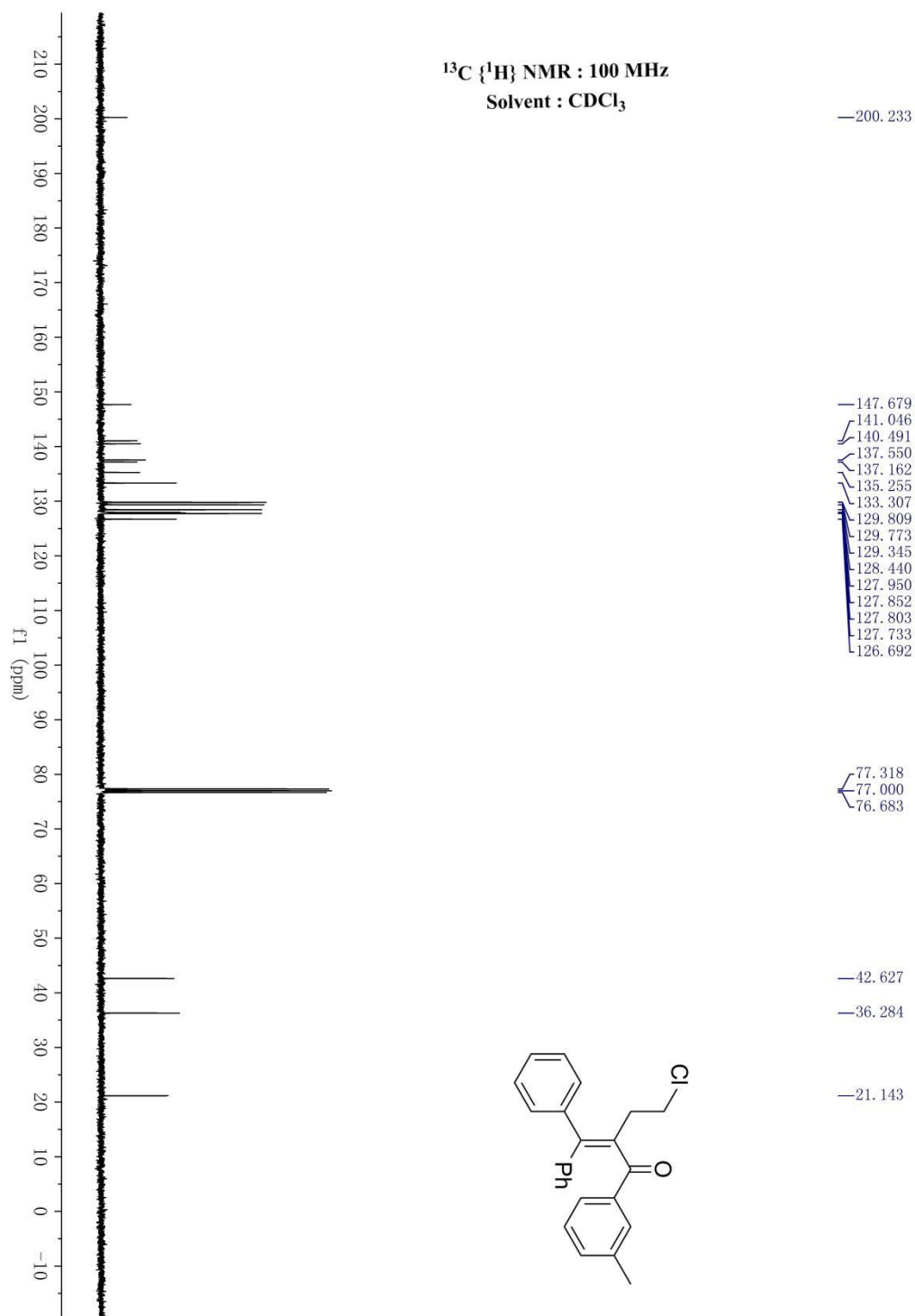
4-Chloro-2-(diphenylmethylene)-1-(3-methoxyphenyl)butan-1-one (3aq)



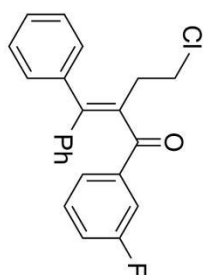
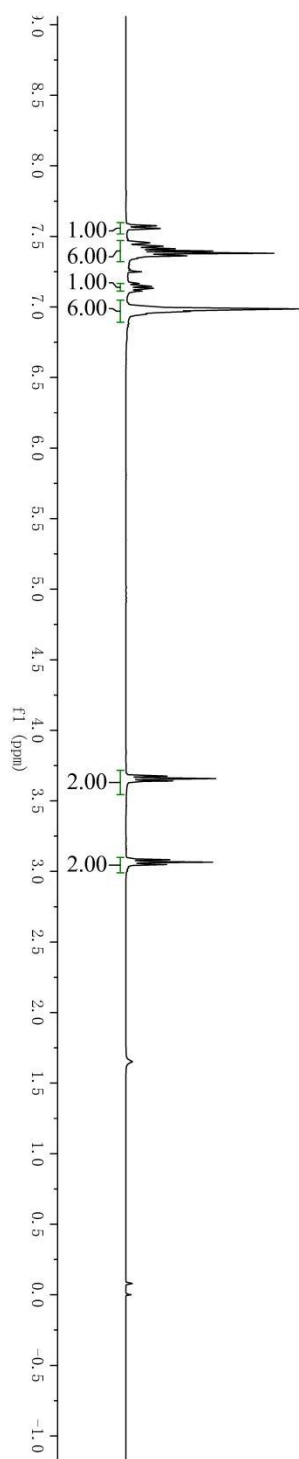


4-chloro-2-(diphenylmethylene)-1-(m-tolyl)butan-1-one (3ar)





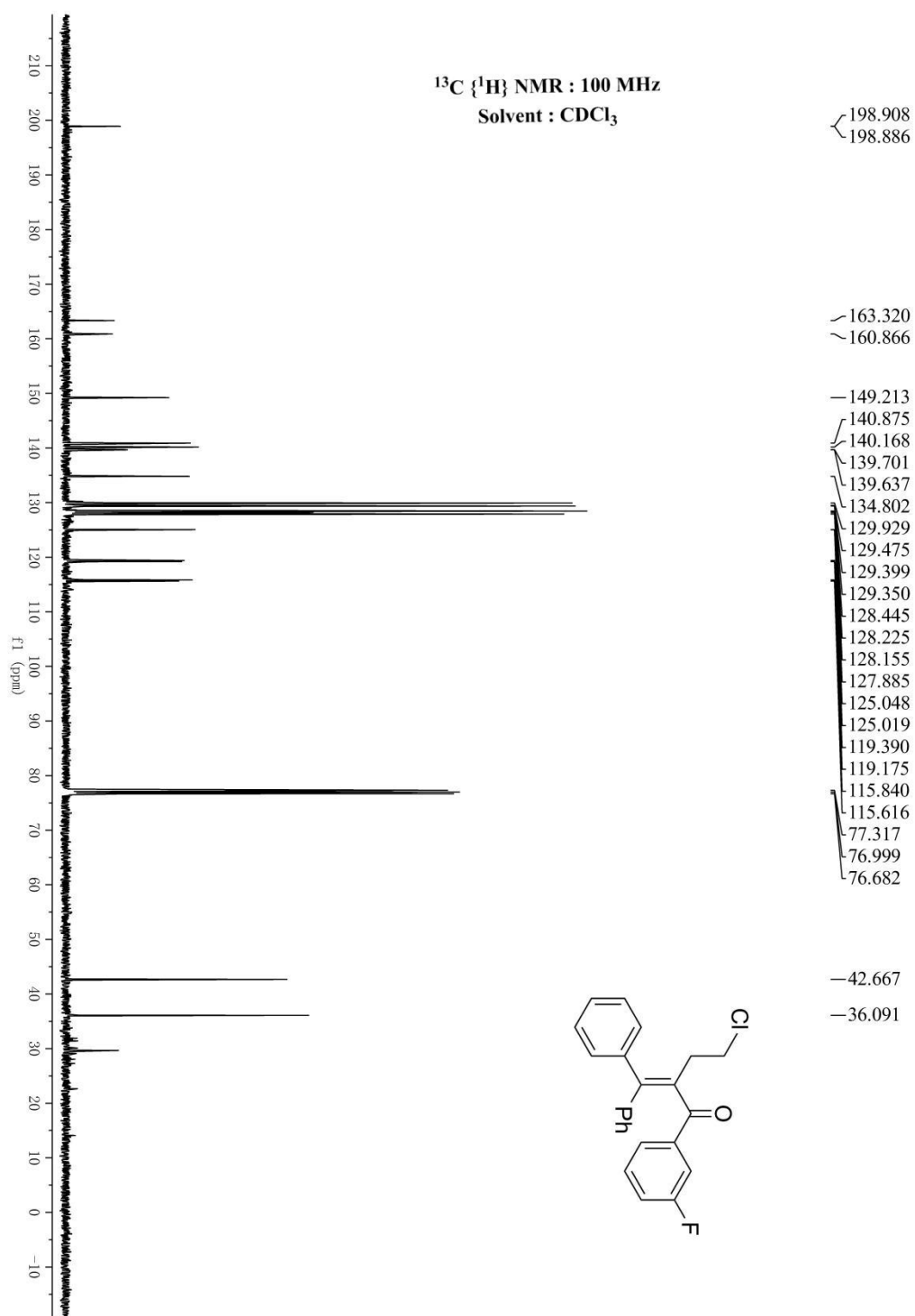
4-chloro-2-(diphenylmethylene)-1-(3-fluorophenyl)butan-1-one (3as)

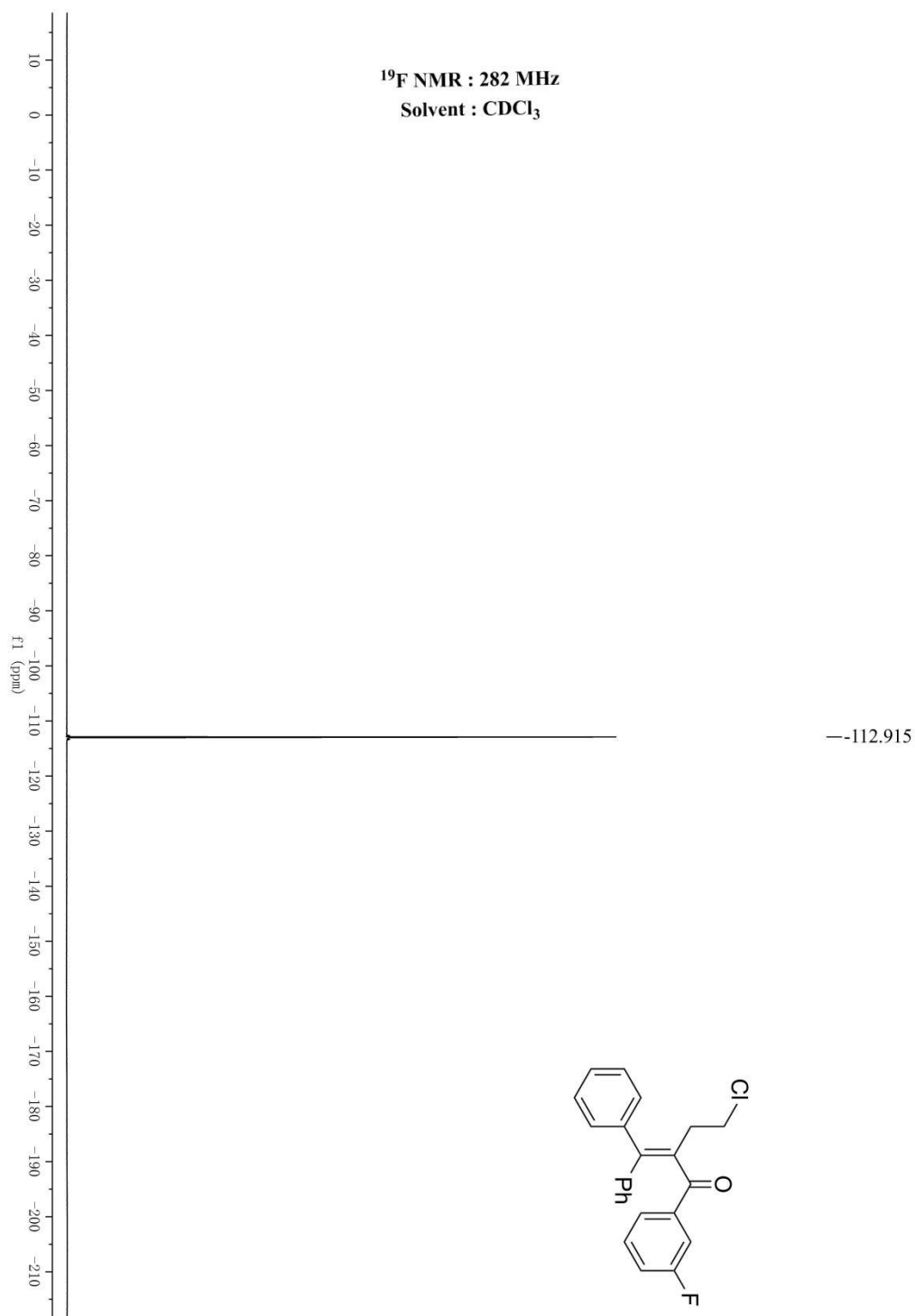


7.577  
7.574  
7.558  
7.555  
7.458  
7.431  
7.413  
7.396  
7.380  
7.362  
7.252  
7.166  
7.152  
7.146  
7.132  
7.126  
7.112  
7.004  
6.991  
6.986  
6.981  
6.970  
6.952  
6.943

3.676  
3.658  
3.641  
3.083  
3.066  
3.049

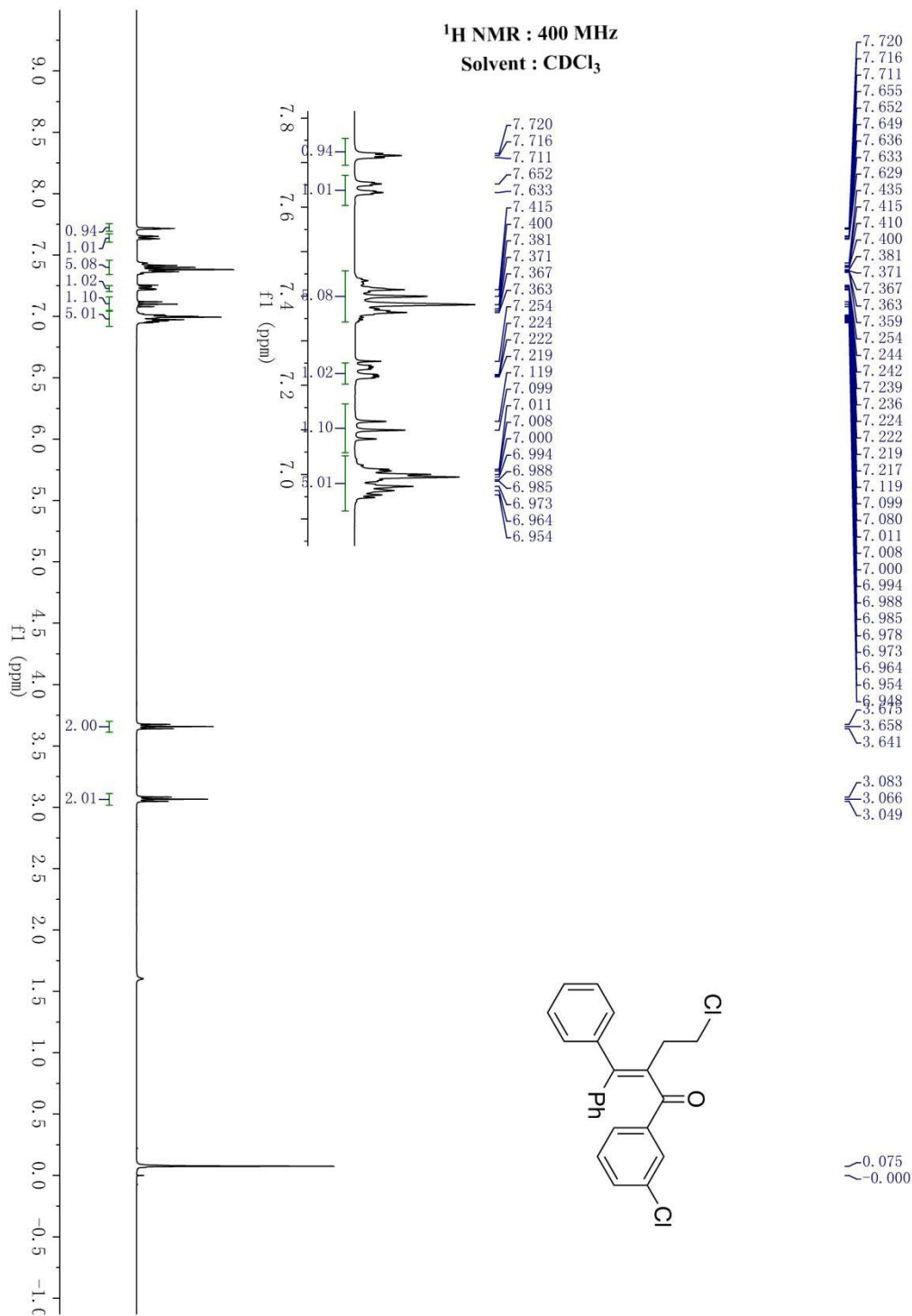
0.080  
0.000

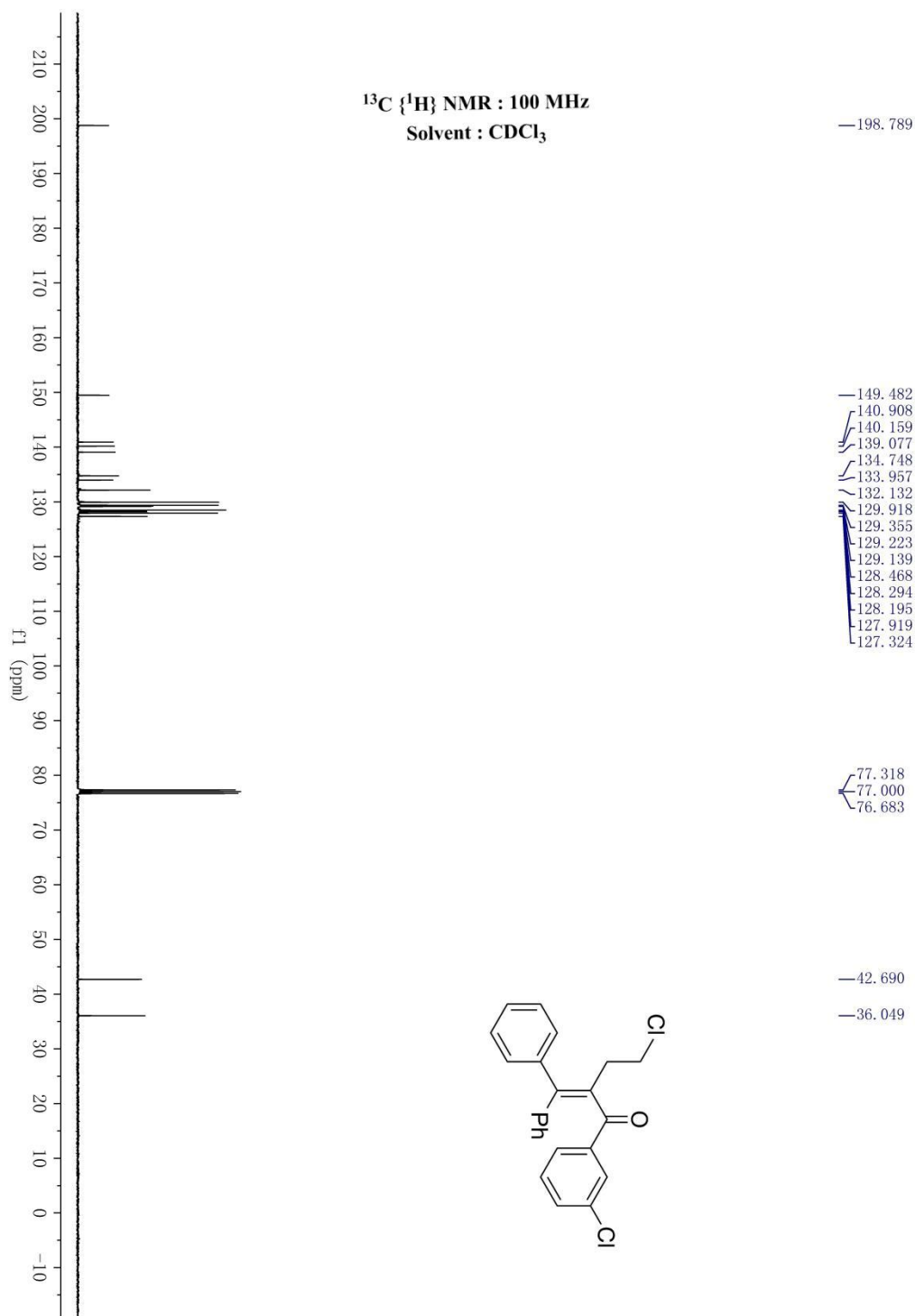




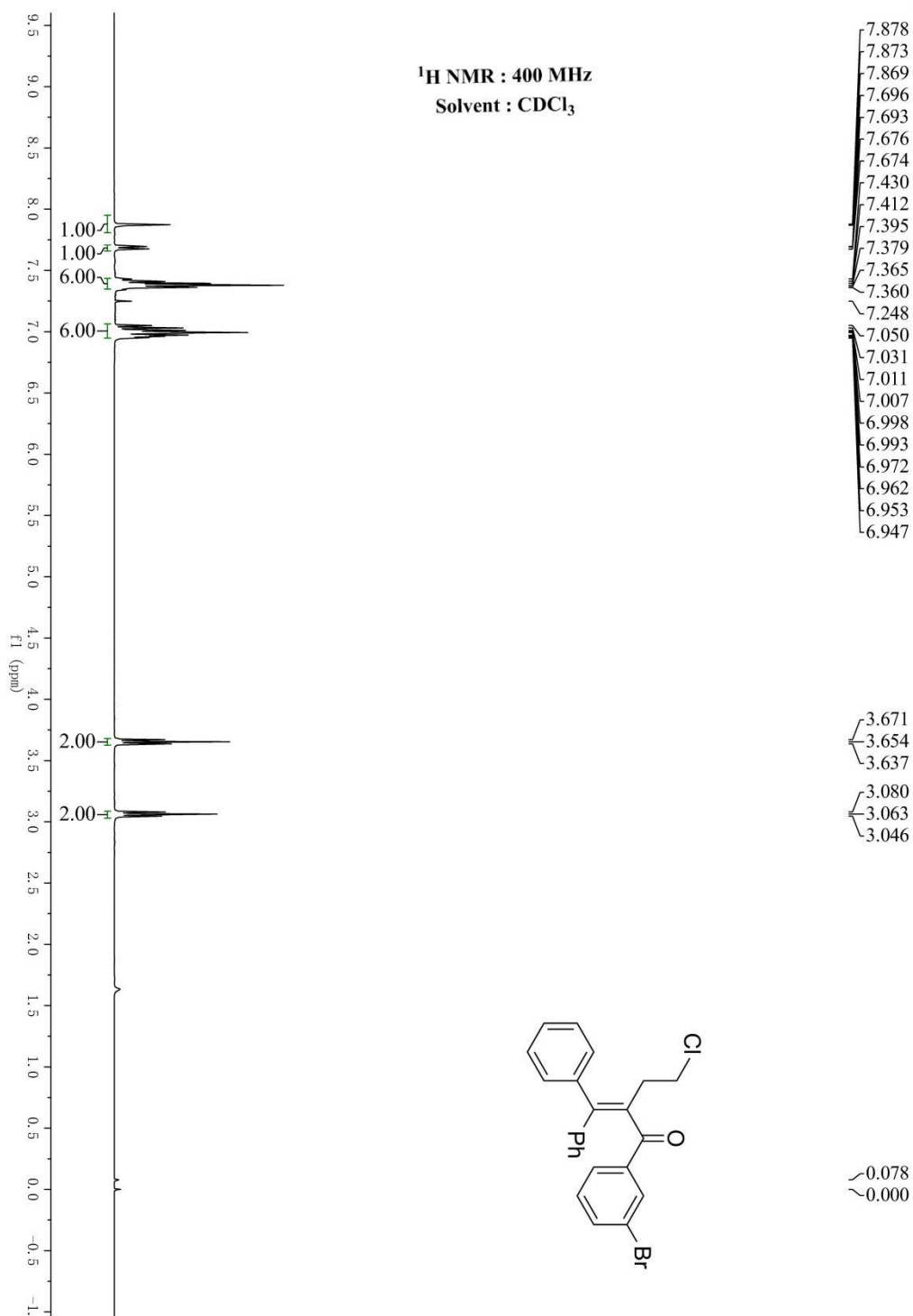
4-chloro-1-(3-chlorophenyl)-2-(diphenylmethylene)butan-1-one (3at)

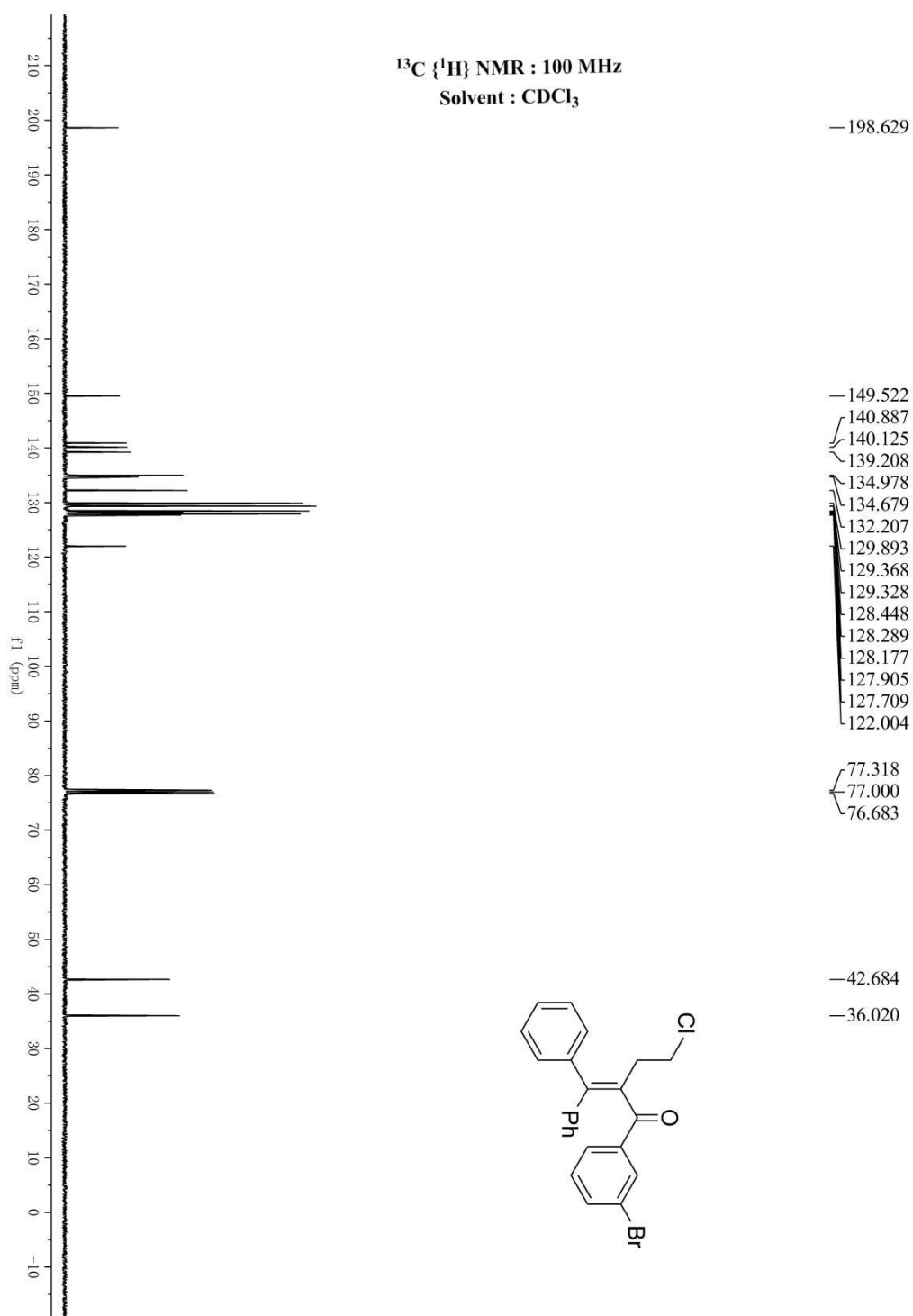




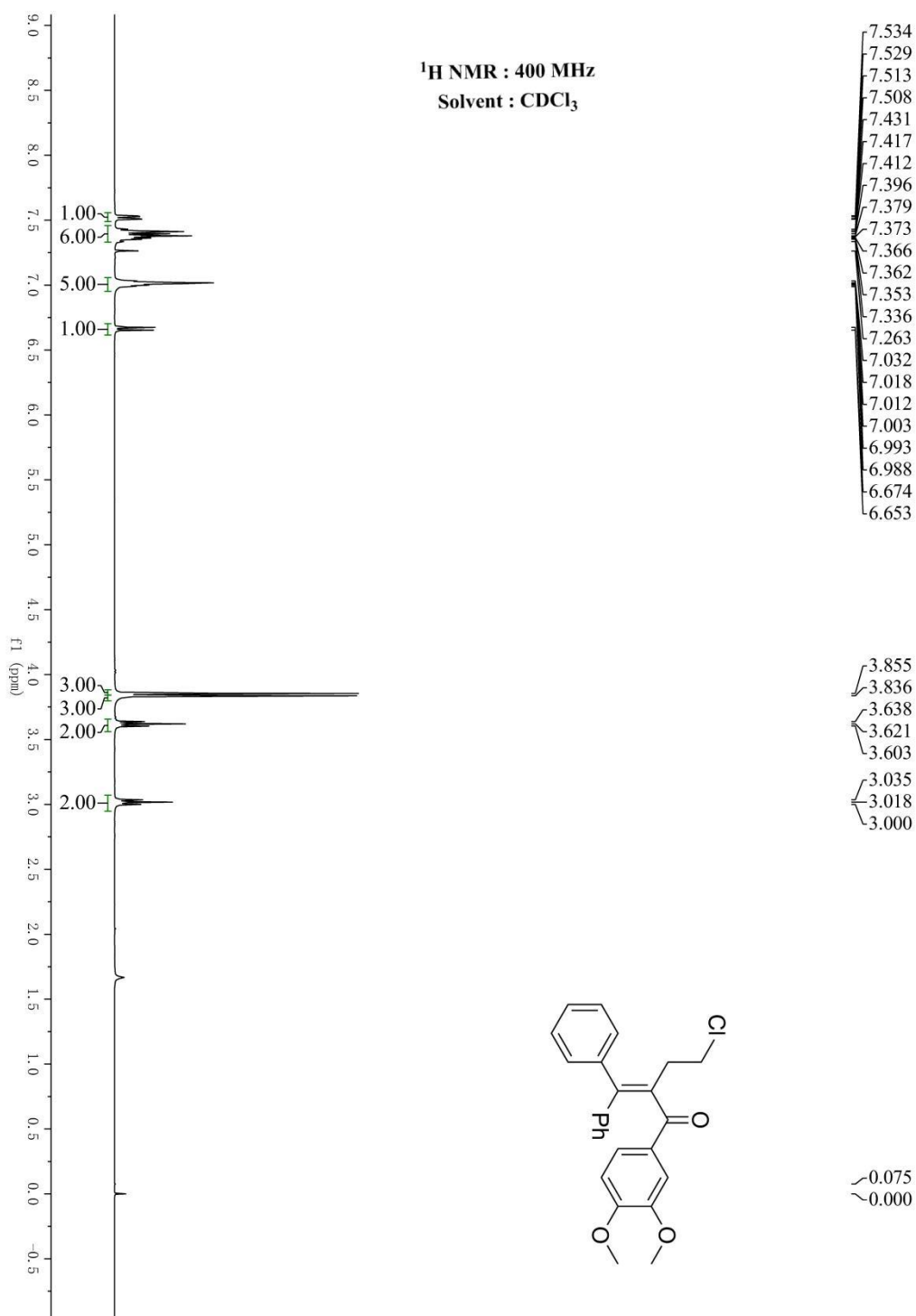


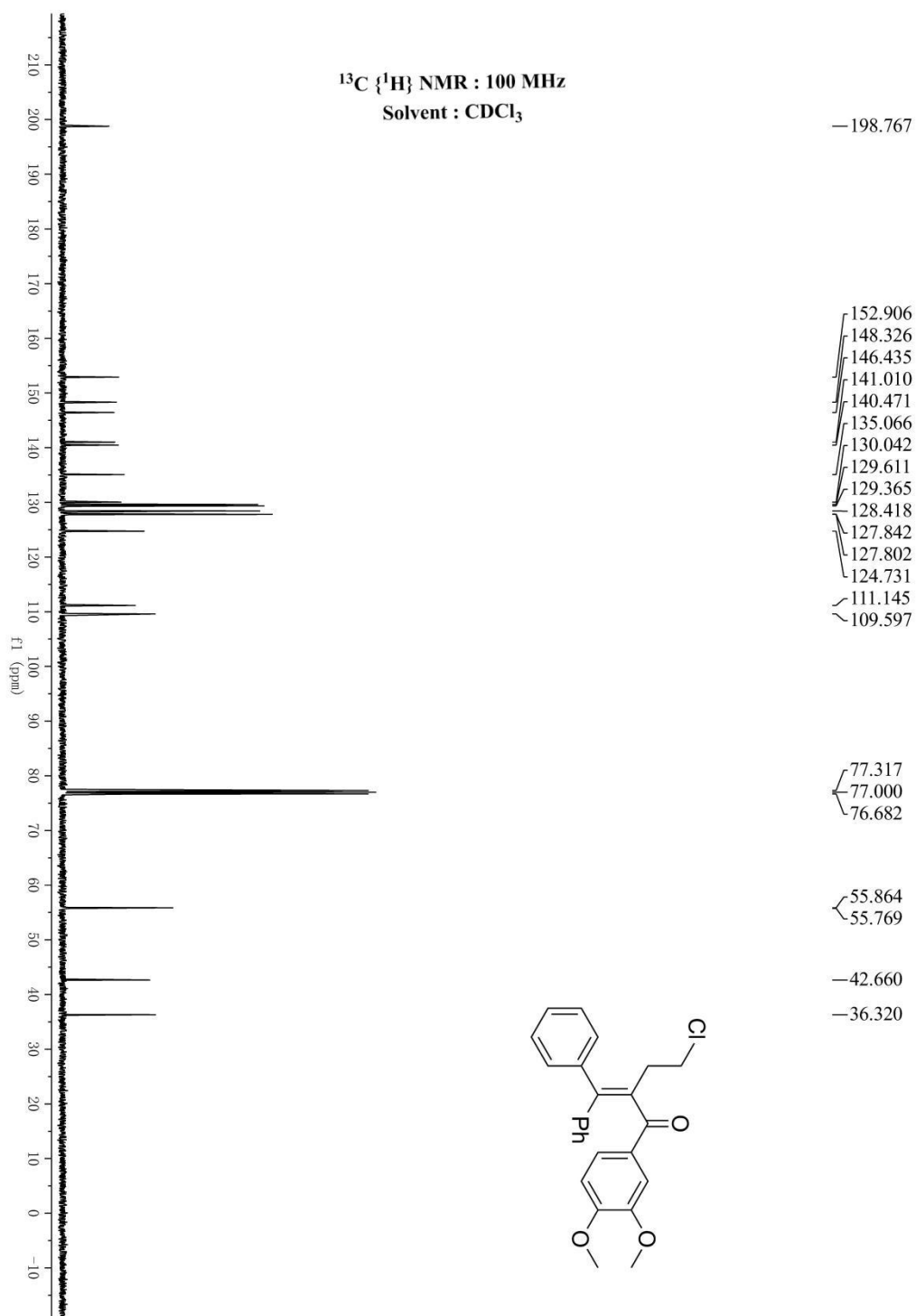
1-(3-Bromophenyl)-4-chloro-2-(diphenylmethylene)butan-1-one (3au)



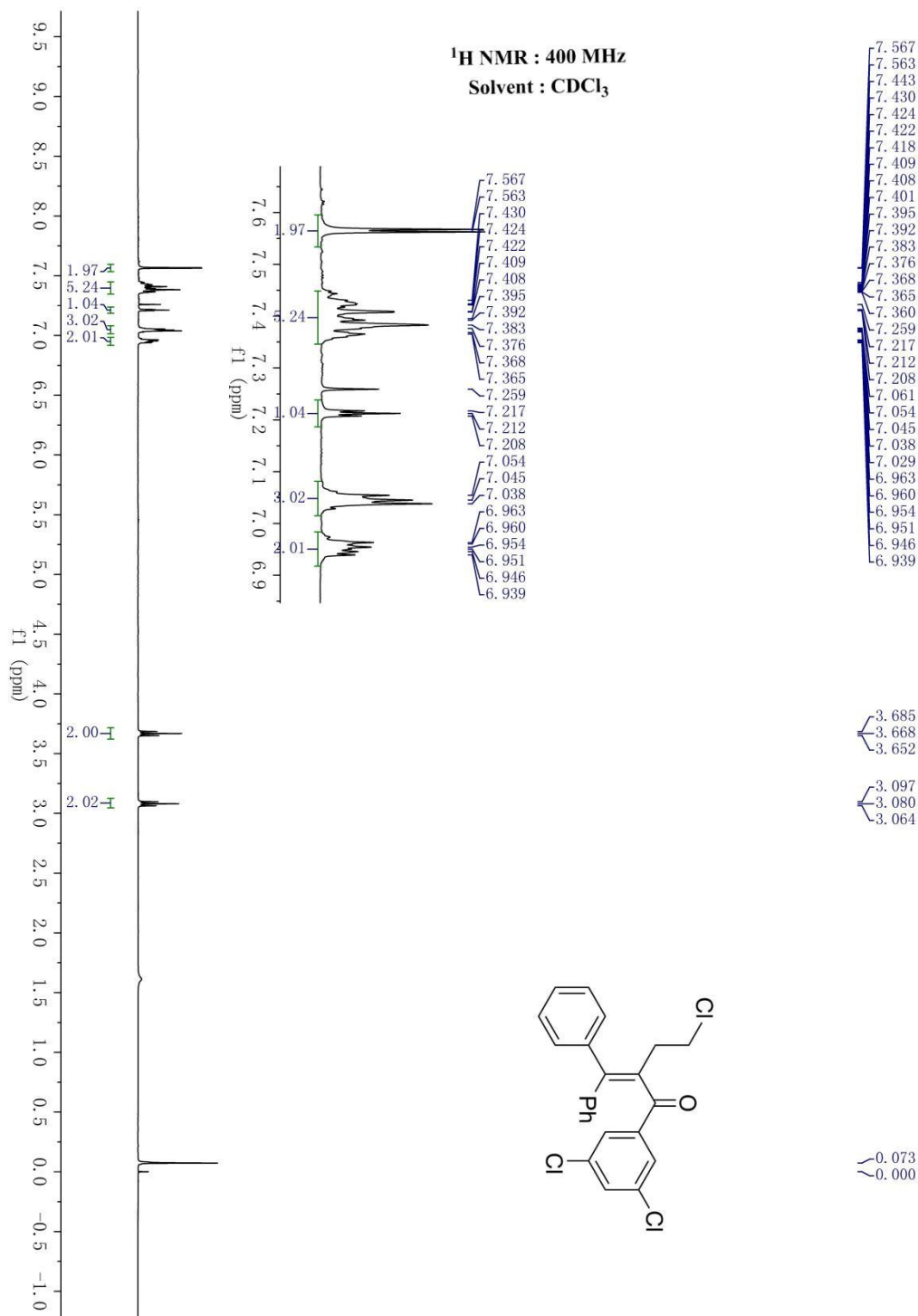


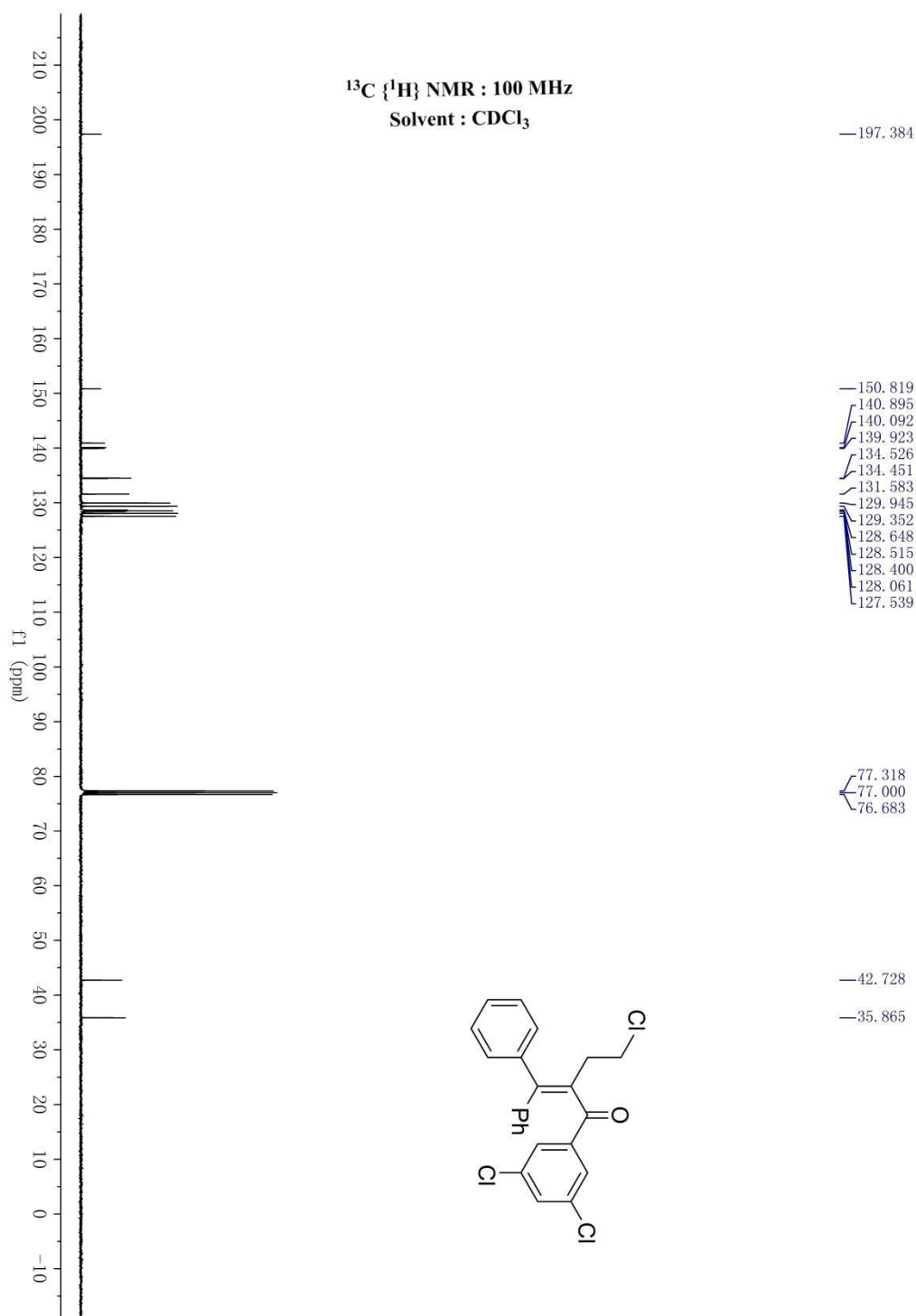
4-chloro-1-(3,4-dimethoxyphenyl)-2-(diphenylmethylene)butan-1-one (3av)





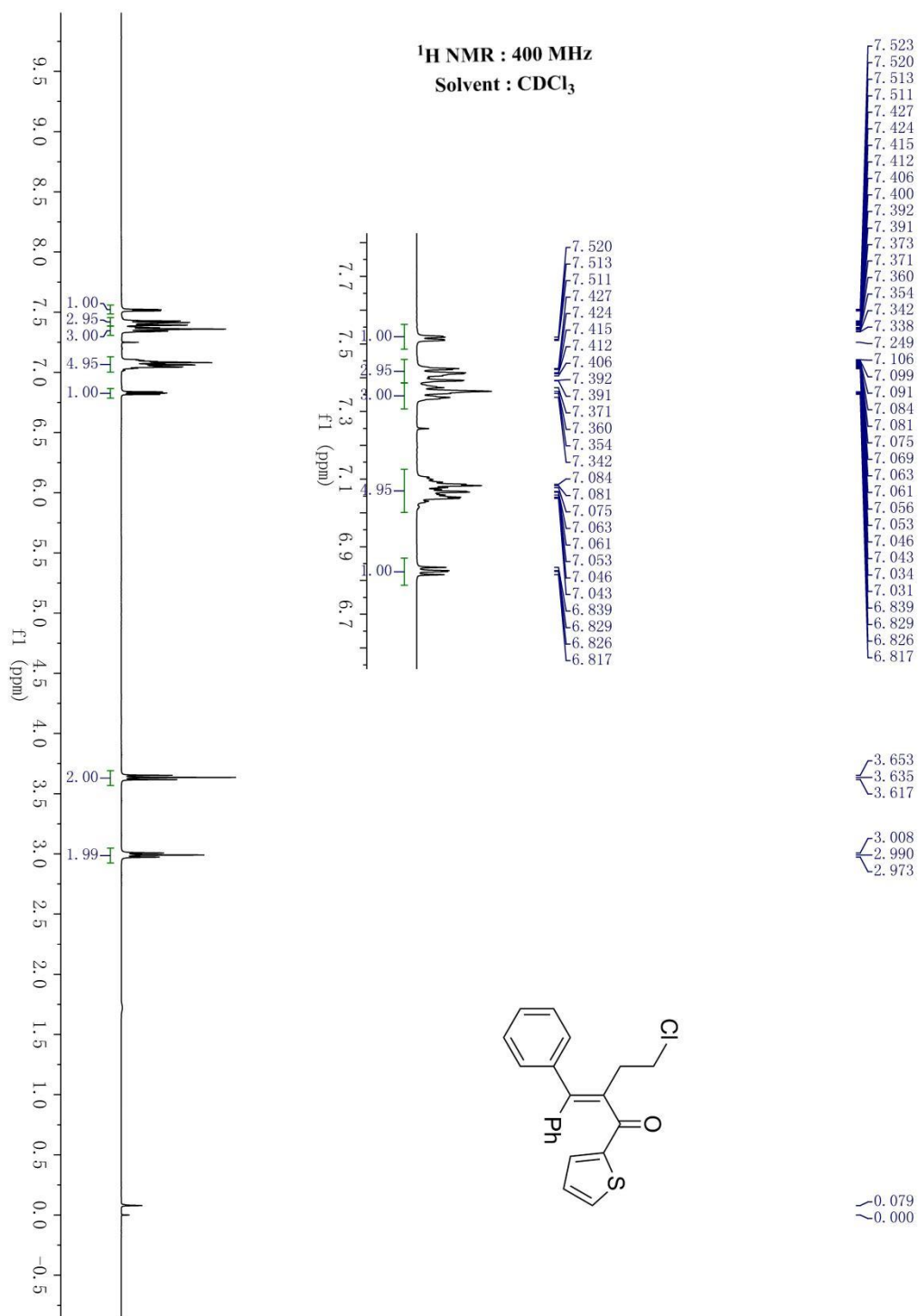
**4-chloro-1-(3,5-dichlorophenyl)-2-(diphenylmethylene)butan-1-one (3aw)**

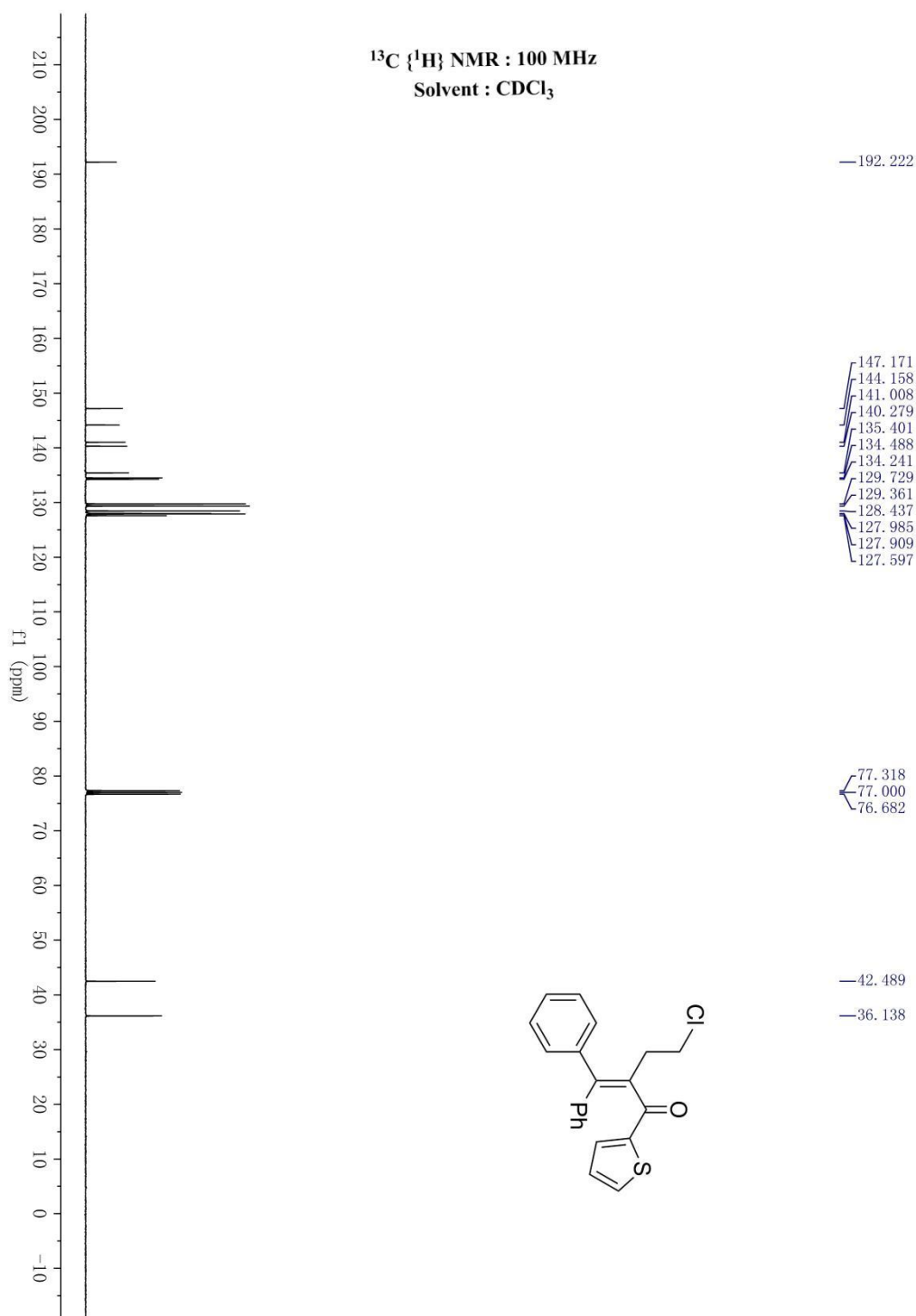




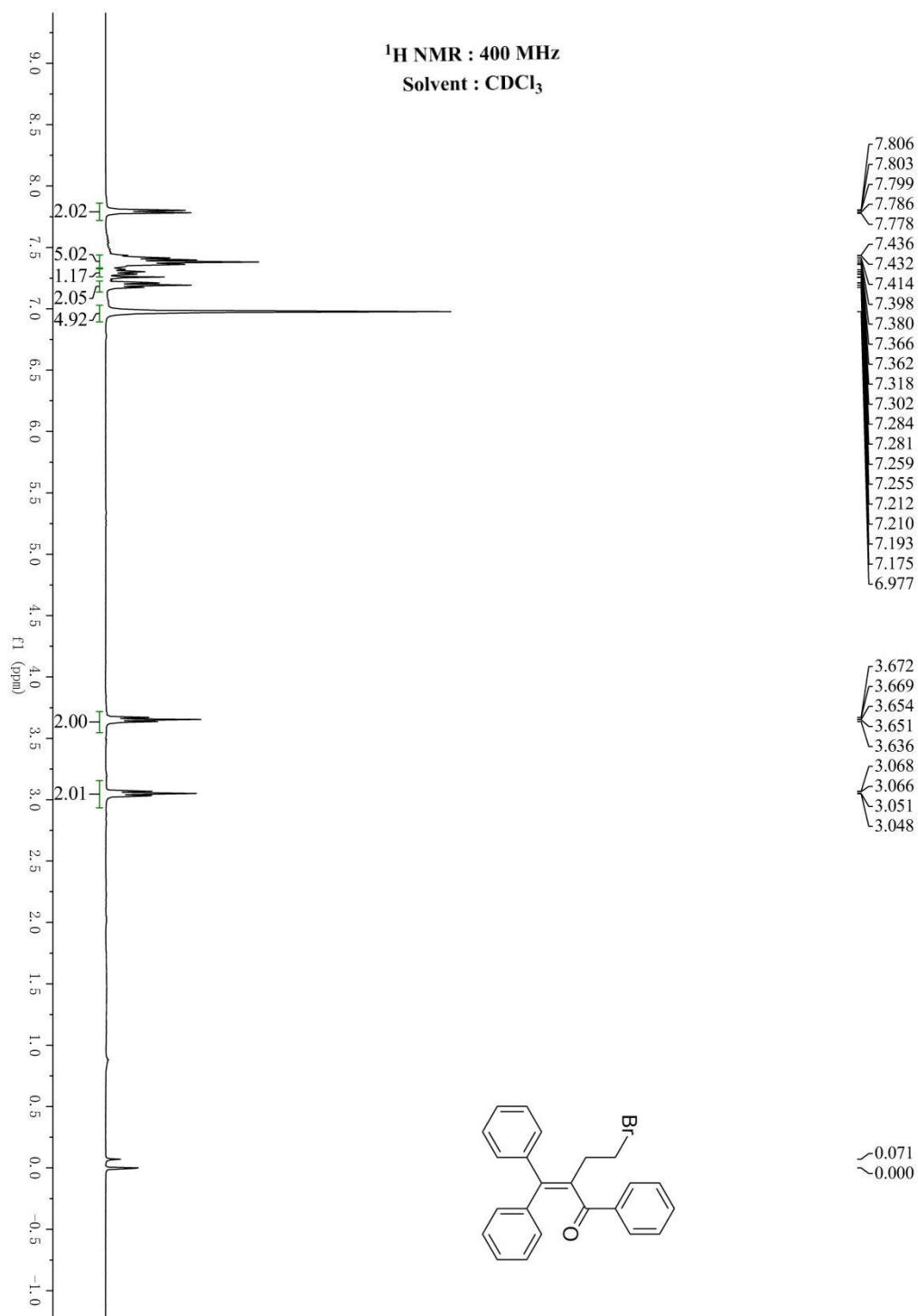
4-chloro-2-(diphenylmethylene)-1-(thiophen-2-yl)butan-1-one (3ax)

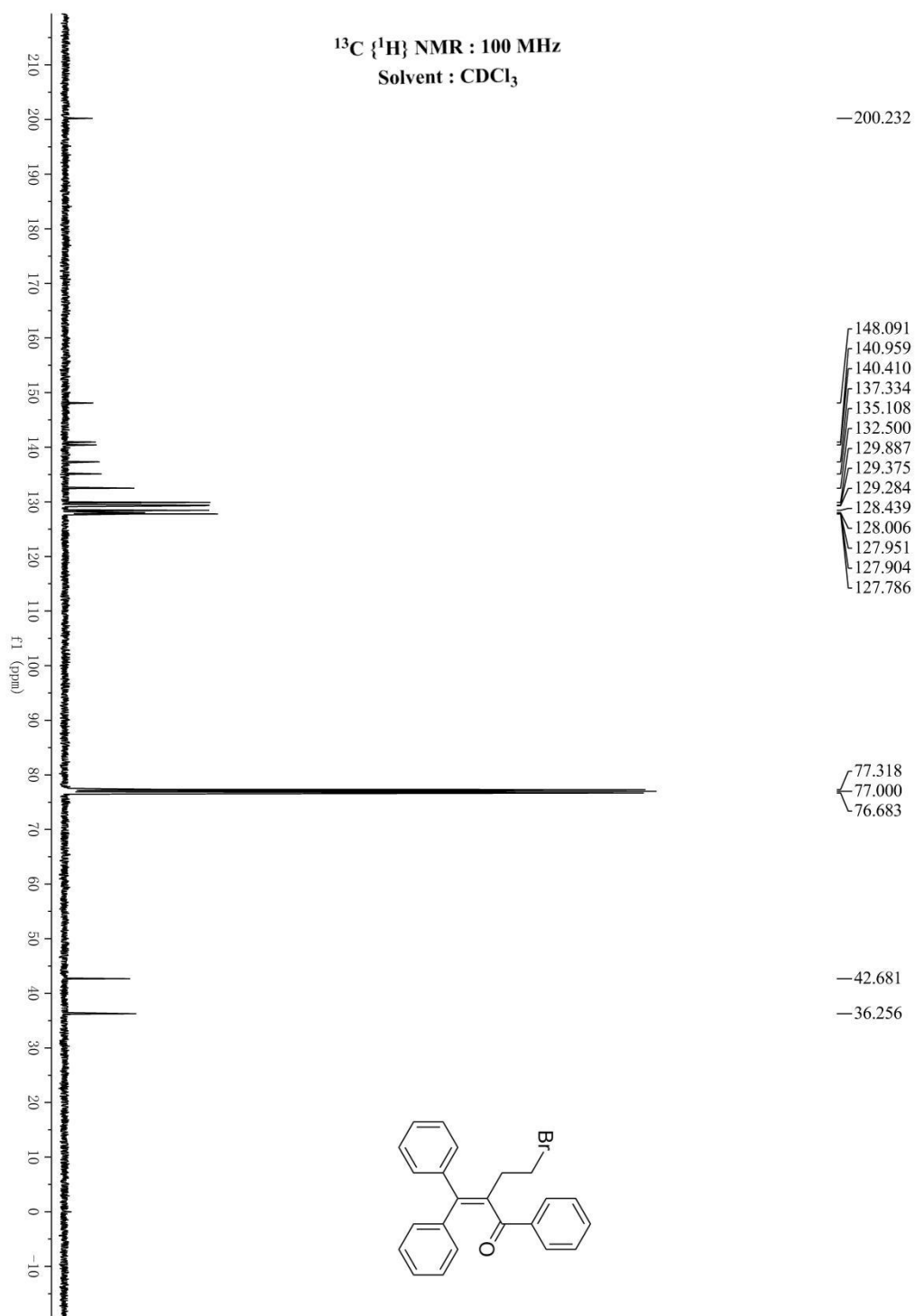




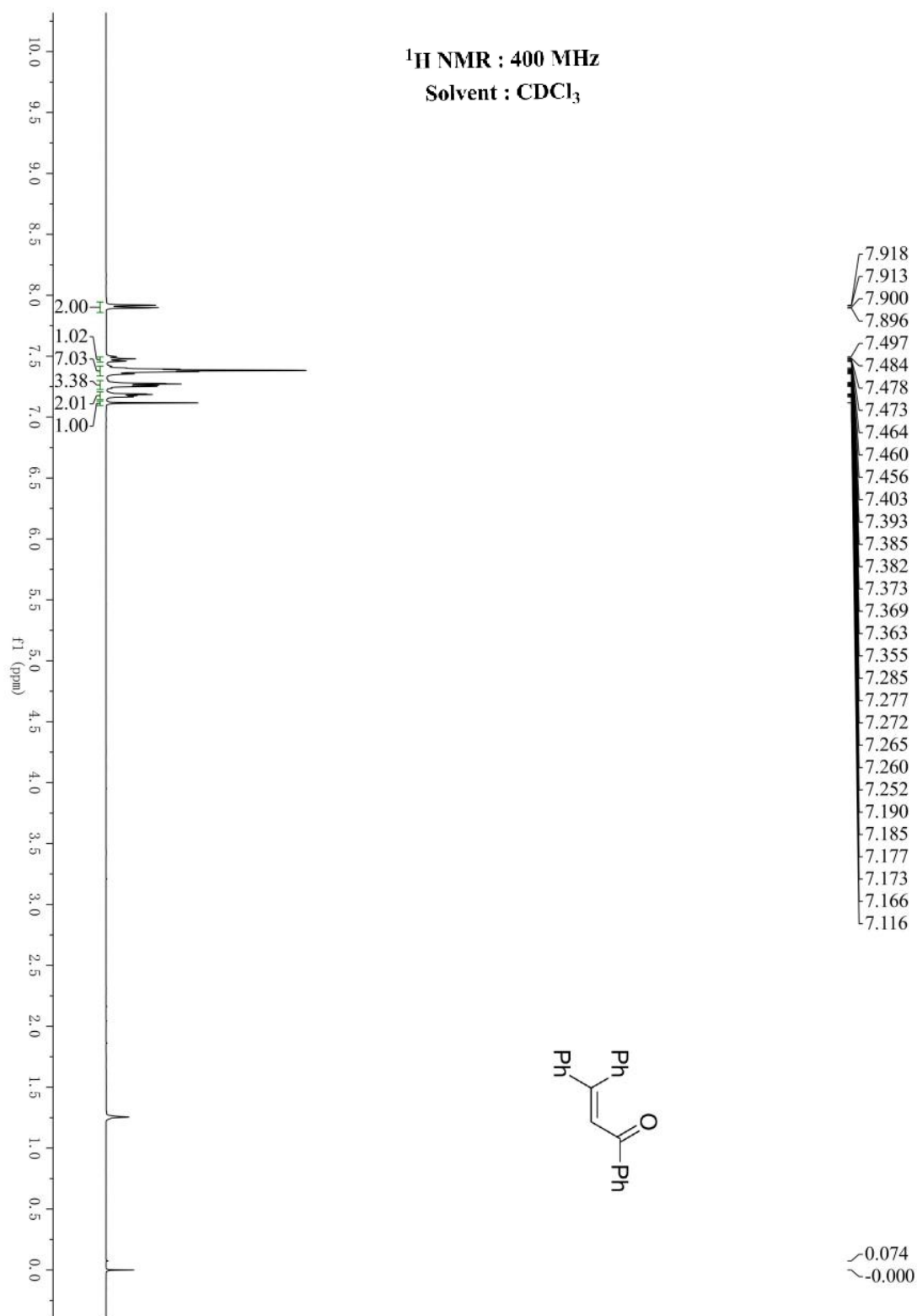


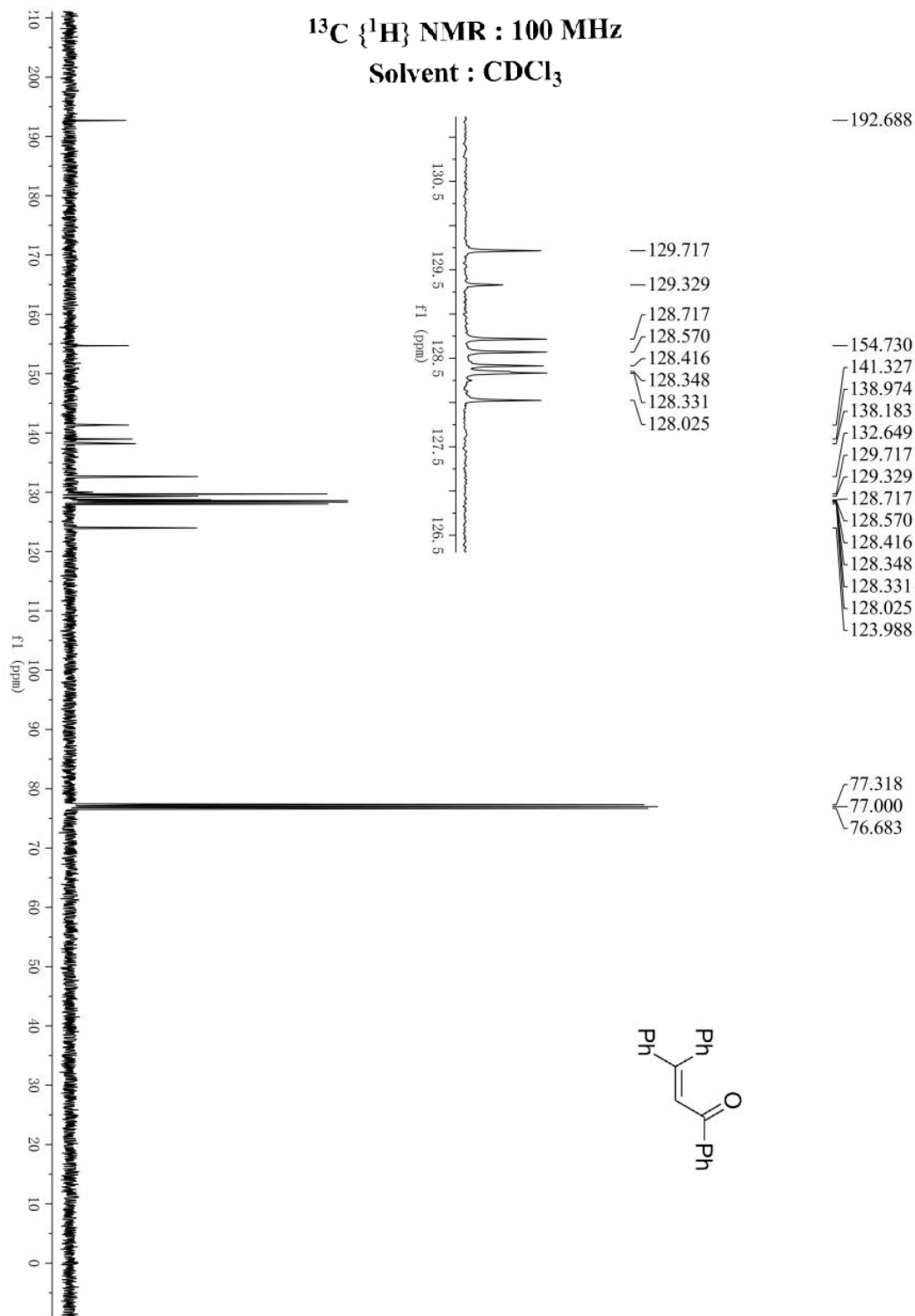
**4-Bromo-2-(diphenylmethylene)-1-phenylbutan-1-one (3ay)**





1,3,3-triphenylprop-2-en-1-one





### 5. The X-ray Single-Crystal Diffraction Analysis of **3ad**

Method for crystal growth: In a vial (25 mL) the product **3ad** was dissolved in dichloromethane (0.2 mL), followed by addition of petroleum ether (2 mL). Then, the big was covered with rubber cap (Don't seal it completely) and was set aside till the crystal formed. The crystal data for **3ad** were integrated using the program SAINT and corrected for absorption effects using the program SADABS. The structures were solved by direct methods and refined on F2 by full-matrix least squares using SHELXTL -2014 software.

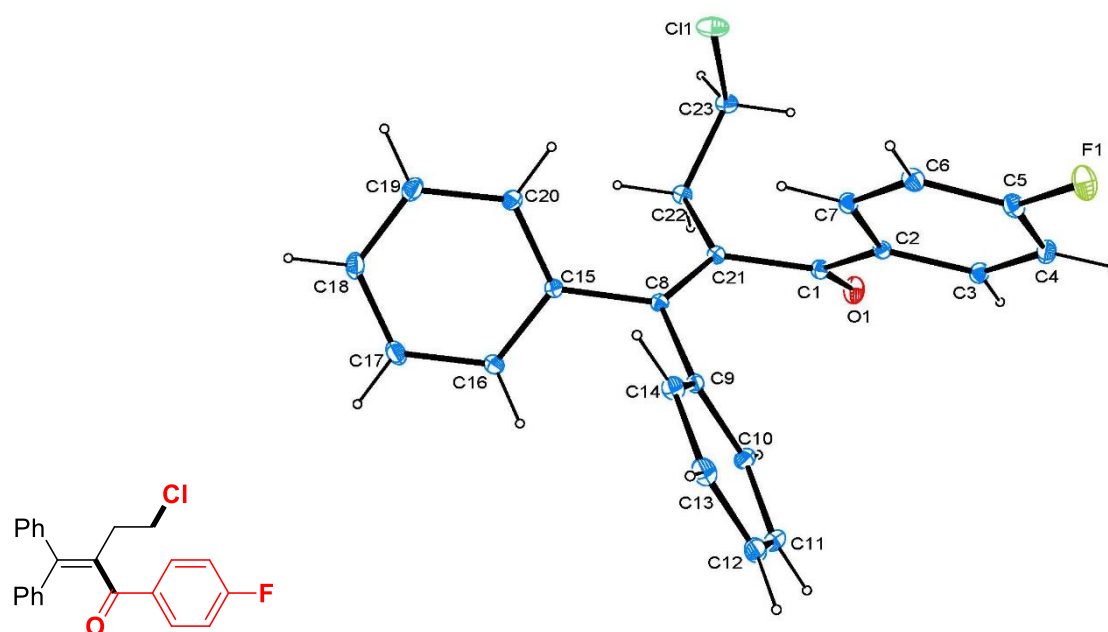


Table S1. Crystal data and structure refinement for liuyu004\_0m.

|                                   |  |
|-----------------------------------|--|
| Identification code               | liuyu004_0m  |
| Empirical formula                 | C <sub>23</sub> H <sub>18</sub> Cl F O   |
| Formula weight                    | 364.82   |
| Temperature                       | 296(2) K   |
| Wavelength                        | 0.71073 Å  |
| Crystal system, space group       | Monoclinic, P2(1)/n  |
| Unit cell dimensions              | a = 11.9234(18) Å    alpha = 90 deg.<br>b = 11.5564(17) Å    beta = 92.537(2) deg.<br>c = 13.594(2) Å    gamma = 90 deg. |
| Volume                            | 1871.2(5) Å <sup>3</sup>   |
| Z, Calculated density             | 4, 1.295 Mg/m <sup>3</sup>   |
| Absorption coefficient            | 0.222 mm <sup>-1</sup>   |
| F(000)                            | 760  |
| Crystal size                      | 0.21 x 0.20 x 0.10 mm  |
| Theta range for data collection   | 2.22 to 27.34 deg.   |
| Limiting indices                  | -14<=h<=15, -14<=k<=8, -17<=l<=16  |
| Reflections collected / unique    | 11028 / 4190 [R(int) = 0.0194]   |
| Completeness to theta = 27.34     | 99.0 %   |
| Absorption correction             | Semi-empirical from equivalents  |
| Max. and min. transmission        | 0.9782 and 0.9549  |
| Refinement method                 | Full-matrix least-squares on F <sup>2</sup>  |
| Data / restraints / parameters    | 4190 / 7 / 236   |
| Goodness-of-fit on F <sup>2</sup> | 1.039  |
| Final R indices [I>2sigma(I)]     | R1 = 0.0472, wR2 = 0.1257  |
| R indices (all data)              | R1 = 0.0611, wR2 = 0.1368  |
| Extinction coefficient            | 0.023(2)   |
| Largest diff. peak and hole       | 0.438 and -0.507 e. Å <sup>-3</sup>  |

Table S2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for liuyu004\_0m.  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

|       | x        | y       | z        | $U(\text{eq})$ |
|-------|----------|---------|----------|----------------|
| O(1)  | 8860(1)  | 9378(1) | 9259(1)  | 72(1)          |
| C(15) | 7646(1)  | 6445(1) | 11403(1) | 41(1)          |
| C(8)  | 7732(1)  | 7083(1) | 10455(1) | 41(1)          |
| C(2)  | 8648(1)  | 7664(1) | 8330(1)  | 44(1)          |
| C(9)  | 6700(1)  | 7023(1) | 9799(1)  | 45(1)          |
| C(21) | 8625(1)  | 7726(1) | 10237(1) | 42(1)          |
| C(7)  | 8702(2)  | 6463(1) | 8309(1)  | 51(1)          |
| C(1)  | 8693(1)  | 8340(1) | 9266(1)  | 48(1)          |
| C(3)  | 8609(2)  | 8266(2) | 7442(1)  | 53(1)          |
| C(22) | 9575(1)  | 8029(2) | 10963(1) | 49(1)          |
| C(6)  | 8702(2)  | 5871(2) | 7427(1)  | 59(1)          |
| C(5)  | 8656(2)  | 6502(2) | 6574(1)  | 60(1)          |
| C(23) | 10745(2) | 7879(2) | 10616(2) | 60(1)          |
| C(14) | 6237(2)  | 5965(2) | 9524(1)  | 60(1)          |
| C(20) | 8404(2)  | 5591(2) | 11691(1) | 55(1)          |
| C(10) | 6149(2)  | 8025(2) | 9505(2)  | 63(1)          |
| C(4)  | 8617(2)  | 7680(2) | 6559(1)  | 62(1)          |
| C(16) | 6760(2)  | 6660(2) | 11999(1) | 57(1)          |
| C(19) | 8283(2)  | 4990(2) | 12561(2) | 72(1)          |
| C(12) | 4701(2)  | 6914(3) | 8677(2)  | 86(1)          |
| C(17) | 6660(2)  | 6065(2) | 12870(2) | 78(1)          |
| C(18) | 7423(2)  | 5237(2) | 13151(2) | 80(1)          |
| C(11) | 5148(2)  | 7967(3) | 8948(2)  | 84(1)          |
| C(13) | 5250(2)  | 5910(2) | 8957(2)  | 77(1)          |
| Cl(1) | 11030(1) | 6417(1) | 10285(1) | 90(1)          |
| F(1)  | 8652(1)  | 5929(1) | 5709(1)  | 94(1)          |



Table S3. Bond lengths [Å] and angles [deg] for liuyu004\_0m.

|                   |            |
|-------------------|------------|
| O(1)-C(1)         | 1.2156(19) |
| C(15)-C(16)       | 1.382(2)   |
| C(15)-C(20)       | 1.383(2)   |
| C(15)-C(8)        | 1.492(2)   |
| C(8)-C(21)        | 1.342(2)   |
| C(8)-C(9)         | 1.488(2)   |
| C(2)-C(7)         | 1.389(2)   |
| C(2)-C(3)         | 1.392(2)   |
| C(2)-C(1)         | 1.492(2)   |
| C(9)-C(10)        | 1.382(2)   |
| C(9)-C(14)        | 1.387(2)   |
| C(21)-C(1)        | 1.504(2)   |
| C(21)-C(22)       | 1.510(2)   |
| C(7)-C(6)         | 1.380(2)   |
| C(7)-H(7)         | 0.9300     |
| C(3)-C(4)         | 1.378(3)   |
| C(3)-H(3)         | 0.9300     |
| C(22)-C(23)       | 1.502(2)   |
| C(22)-H(22A)      | 0.9700     |
| C(22)-H(22B)      | 0.9700     |
| C(6)-C(5)         | 1.370(3)   |
| C(6)-H(6)         | 0.9300     |
| C(5)-F(1)         | 1.349(2)   |
| C(5)-C(4)         | 1.362(3)   |
| C(23)-Cl(1)       | 1.7853(19) |
| C(23)-H(23A)      | 0.9700     |
| C(23)-H(23B)      | 0.9700     |
| C(14)-C(13)       | 1.379(3)   |
| C(14)-H(14)       | 0.9300     |
| C(20)-C(19)       | 1.384(3)   |
| C(20)-H(20)       | 0.9300     |
| C(10)-C(11)       | 1.386(3)   |
| C(10)-H(10)       | 0.9300     |
| C(4)-H(4)         | 0.9300     |
| C(16)-C(17)       | 1.379(3)   |
| C(16)-H(16)       | 0.9300     |
| C(19)-C(18)       | 1.360(3)   |
| C(19)-H(19)       | 0.9300     |
| C(12)-C(11)       | 1.373(4)   |
| C(12)-C(13)       | 1.378(4)   |
| C(12)-H(12)       | 0.9300     |
| C(17)-C(18)       | 1.363(3)   |
| C(17)-H(17)       | 0.9300     |
| C(18)-H(18)       | 0.9300     |
| C(11)-H(11)       | 0.9300     |
| C(13)-H(13)       | 0.9300     |
| C(16)-C(15)-C(20) | 117.96(15) |
| C(16)-C(15)-C(8)  | 120.05(14) |
| C(20)-C(15)-C(8)  | 121.91(14) |

---

|                     |            |
|---------------------|------------|
| C(21)-C(8)-C(9)     | 122.44(14) |
| C(21)-C(8)-C(15)    | 123.33(14) |
| C(9)-C(8)-C(15)     | 114.05(12) |
| C(7)-C(2)-C(3)      | 118.76(15) |
| C(7)-C(2)-C(1)      | 122.73(14) |
| C(3)-C(2)-C(1)      | 118.43(15) |
| C(10)-C(9)-C(14)    | 118.80(17) |
| C(10)-C(9)-C(8)     | 120.26(15) |
| C(14)-C(9)-C(8)     | 120.81(15) |
| C(8)-C(21)-C(1)     | 121.94(14) |
| C(8)-C(21)-C(22)    | 124.28(15) |
| C(1)-C(21)-C(22)    | 113.36(13) |
| C(6)-C(7)-C(2)      | 121.00(16) |
| C(6)-C(7)-H(7)      | 119.5      |
| C(2)-C(7)-H(7)      | 119.5      |
| O(1)-C(1)-C(2)      | 120.64(15) |
| O(1)-C(1)-C(21)     | 119.15(15) |
| C(2)-C(1)-C(21)     | 120.02(13) |
| C(4)-C(3)-C(2)      | 120.48(17) |
| C(4)-C(3)-H(3)      | 119.8      |
| C(2)-C(3)-H(3)      | 119.8      |
| C(23)-C(22)-C(21)   | 116.61(15) |
| C(23)-C(22)-H(22A)  | 108.1      |
| C(21)-C(22)-H(22A)  | 108.1      |
| C(23)-C(22)-H(22B)  | 108.1      |
| C(21)-C(22)-H(22B)  | 108.1      |
| H(22A)-C(22)-H(22B) | 107.3      |
| C(5)-C(6)-C(7)      | 118.08(17) |
| C(5)-C(6)-H(6)      | 121.0      |
| C(7)-C(6)-H(6)      | 121.0      |
| F(1)-C(5)-C(4)      | 118.65(18) |
| F(1)-C(5)-C(6)      | 118.41(18) |
| C(4)-C(5)-C(6)      | 122.94(17) |
| C(22)-C(23)-Cl(1)   | 112.25(12) |
| C(22)-C(23)-H(23A)  | 109.2      |
| Cl(1)-C(23)-H(23A)  | 109.2      |
| C(22)-C(23)-H(23B)  | 109.2      |
| Cl(1)-C(23)-H(23B)  | 109.2      |
| H(23A)-C(23)-H(23B) | 107.9      |
| C(13)-C(14)-C(9)    | 120.8(2)   |
| C(13)-C(14)-H(14)   | 119.6      |
| C(9)-C(14)-H(14)    | 119.6      |
| C(15)-C(20)-C(19)   | 120.59(17) |
| C(15)-C(20)-H(20)   | 119.7      |
| C(19)-C(20)-H(20)   | 119.7      |
| C(9)-C(10)-C(11)    | 120.3(2)   |
| C(9)-C(10)-H(10)    | 119.9      |
| C(11)-C(10)-H(10)   | 119.9      |
| C(5)-C(4)-C(3)      | 118.74(17) |
| C(5)-C(4)-H(4)      | 120.6      |
| C(3)-C(4)-H(4)      | 120.6      |
| C(17)-C(16)-C(15)   | 120.74(19) |

---

|                   |            |
|-------------------|------------|
| C(17)-C(16)-H(16) | 119.6      |
| C(15)-C(16)-H(16) | 119.6      |
| C(18)-C(19)-C(20) | 120.51(19) |
| C(18)-C(19)-H(19) | 119.7      |
| C(20)-C(19)-H(19) | 119.7      |
| C(11)-C(12)-C(13) | 119.87(19) |
| C(11)-C(12)-H(12) | 120.1      |
| C(13)-C(12)-H(12) | 120.1      |
| C(18)-C(17)-C(16) | 120.6(2)   |
| C(18)-C(17)-H(17) | 119.7      |
| C(16)-C(17)-H(17) | 119.7      |
| C(19)-C(18)-C(17) | 119.59(19) |
| C(19)-C(18)-H(18) | 120.2      |
| C(17)-C(18)-H(18) | 120.2      |
| C(12)-C(11)-C(10) | 120.3(2)   |
| C(12)-C(11)-H(11) | 119.8      |
| C(10)-C(11)-H(11) | 119.8      |
| C(12)-C(13)-C(14) | 119.9(2)   |
| C(12)-C(13)-H(13) | 120.0      |
| C(14)-C(13)-H(13) | 120.0      |

---

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for liuyu004\_0m. The anisotropic displacement factor exponent takes the form:  $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

|       | U11    | U22    | U33    | U23    | U13    | U12    |
|-------|--------|--------|--------|--------|--------|--------|
| O(1)  | 107(1) | 39(1)  | 71(1)  | 3(1)   | 7(1)   | -17(1) |
| C(15) | 41(1)  | 39(1)  | 43(1)  | -2(1)  | 0(1)   | -5(1)  |
| C(8)  | 43(1)  | 35(1)  | 44(1)  | -2(1)  | 3(1)   | 1(1)   |
| C(2)  | 39(1)  | 44(1)  | 50(1)  | 4(1)   | 4(1)   | -3(1)  |
| C(9)  | 43(1)  | 50(1)  | 41(1)  | 4(1)   | 4(1)   | -4(1)  |
| C(21) | 45(1)  | 37(1)  | 46(1)  | -3(1)  | 3(1)   | -2(1)  |
| C(7)  | 55(1)  | 45(1)  | 52(1)  | 4(1)   | 10(1)  | 0(1)   |
| C(1)  | 48(1)  | 41(1)  | 55(1)  | 3(1)   | 5(1)   | -5(1)  |
| C(3)  | 54(1)  | 50(1)  | 56(1)  | 9(1)   | 2(1)   | -3(1)  |
| C(22) | 48(1)  | 46(1)  | 54(1)  | -7(1)  | 1(1)   | -5(1)  |
| C(6)  | 65(1)  | 49(1)  | 65(1)  | -6(1)  | 12(1)  | -1(1)  |
| C(5)  | 58(1)  | 69(1)  | 52(1)  | -8(1)  | 7(1)   | -8(1)  |
| C(23) | 49(1)  | 52(1)  | 77(1)  | -4(1)  | 1(1)   | -4(1)  |
| C(14) | 56(1)  | 61(1)  | 62(1)  | -5(1)  | 0(1)   | -13(1) |
| C(20) | 56(1)  | 48(1)  | 62(1)  | 6(1)   | 5(1)   | 4(1)   |
| C(10) | 58(1)  | 63(1)  | 67(1)  | 14(1)  | -2(1)  | 4(1)   |
| C(4)  | 64(1)  | 74(1)  | 49(1)  | 11(1)  | 0(1)   | -6(1)  |
| C(16) | 49(1)  | 69(1)  | 55(1)  | 2(1)   | 8(1)   | 3(1)   |
| C(19) | 65(1)  | 66(1)  | 84(1)  | 29(1)  | -10(1) | -8(1)  |
| C(12) | 53(1)  | 154(3) | 49(1)  | 12(1)  | -8(1)  | -15(1) |
| C(17) | 61(1)  | 119(2) | 55(1)  | 11(1)  | 15(1)  | -9(1)  |
| C(18) | 64(1)  | 111(2) | 64(1)  | 37(1)  | -9(1)  | -30(1) |
| C(11) | 63(1)  | 115(2) | 74(1)  | 33(1)  | -8(1)  | 15(1)  |
| C(13) | 66(1)  | 106(2) | 58(1)  | -13(1) | -1(1)  | -31(1) |
| Cl(1) | 66(1)  | 68(1)  | 136(1) | -32(1) | -1(1)  | 13(1)  |
| F(1)  | 128(1) | 96(1)  | 59(1)  | -21(1) | 15(1)  | -19(1) |

Table S5. Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for liuyu004\_0m.

|        | x     | y    | z     | U(eq) |
|--------|-------|------|-------|-------|
| H(7)   | 8739  | 6053 | 8898  | 61    |
| H(3)   | 8577  | 9071 | 7444  | 64    |
| H(22A) | 9485  | 8829 | 11159 | 59    |
| H(22B) | 9501  | 7556 | 11547 | 59    |
| H(6)   | 8732  | 5067 | 7414  | 71    |
| H(23A) | 11279 | 8119 | 11135 | 71    |
| H(23B) | 10844 | 8375 | 10051 | 71    |
| H(14)  | 6596  | 5284 | 9724  | 72    |
| H(20)  | 8999  | 5418 | 11297 | 66    |
| H(10)  | 6451  | 8742 | 9681  | 75    |
| H(4)   | 8596  | 8080 | 5966  | 75    |
| H(16)  | 6225  | 7212 | 11810 | 69    |
| H(19)  | 8794  | 4412 | 12743 | 86    |
| H(12)  | 4028  | 6878 | 8305  | 103   |
| H(17)  | 6067  | 6230 | 13269 | 94    |
| H(18)  | 7356  | 4845 | 13743 | 96    |
| H(11)  | 4778  | 8645 | 8758  | 101   |
| H(13)  | 4957  | 5195 | 8763  | 92    |

Table S6. Torsion angles [deg] for liuyu004\_0m.

---

|                         |             |
|-------------------------|-------------|
| C(16)-C(15)-C(8)-C(21)  | 122.58(18)  |
| C(20)-C(15)-C(8)-C(21)  | -60.7(2)    |
| C(16)-C(15)-C(8)-C(9)   | -52.81(19)  |
| C(20)-C(15)-C(8)-C(9)   | 123.92(16)  |
| C(21)-C(8)-C(9)-C(10)   | -54.2(2)    |
| C(15)-C(8)-C(9)-C(10)   | 121.24(16)  |
| C(21)-C(8)-C(9)-C(14)   | 129.83(17)  |
| C(15)-C(8)-C(9)-C(14)   | -54.7(2)    |
| C(9)-C(8)-C(21)-C(1)    | -6.2(2)     |
| C(15)-C(8)-C(21)-C(1)   | 178.81(14)  |
| C(9)-C(8)-C(21)-C(22)   | 165.87(14)  |
| C(15)-C(8)-C(21)-C(22)  | -9.1(2)     |
| C(3)-C(2)-C(7)-C(6)     | -0.8(2)     |
| C(1)-C(2)-C(7)-C(6)     | -177.46(15) |
| C(7)-C(2)-C(1)-O(1)     | 165.80(17)  |
| C(3)-C(2)-C(1)-O(1)     | -10.8(2)    |
| C(7)-C(2)-C(1)-C(21)    | -9.2(2)     |
| C(3)-C(2)-C(1)-C(21)    | 174.15(14)  |
| C(8)-C(21)-C(1)-O(1)    | 124.69(18)  |
| C(22)-C(21)-C(1)-O(1)   | -48.2(2)    |
| C(8)-C(21)-C(1)-C(2)    | -60.2(2)    |
| C(22)-C(21)-C(1)-C(2)   | 126.94(15)  |
| C(7)-C(2)-C(3)-C(4)     | 0.4(2)      |
| C(1)-C(2)-C(3)-C(4)     | 177.12(16)  |
| C(8)-C(21)-C(22)-C(23)  | 133.65(17)  |
| C(1)-C(21)-C(22)-C(23)  | -53.70(19)  |
| C(2)-C(7)-C(6)-C(5)     | 0.5(3)      |
| C(7)-C(6)-C(5)-F(1)     | -179.78(17) |
| C(7)-C(6)-C(5)-C(4)     | 0.3(3)      |
| C(21)-C(22)-C(23)-Cl(1) | -60.48(19)  |
| C(10)-C(9)-C(14)-C(13)  | 0.7(3)      |
| C(8)-C(9)-C(14)-C(13)   | 176.74(16)  |
| C(16)-C(15)-C(20)-C(19) | -1.3(3)     |
| C(8)-C(15)-C(20)-C(19)  | -178.05(16) |
| C(14)-C(9)-C(10)-C(11)  | 0.3(3)      |
| C(8)-C(9)-C(10)-C(11)   | -175.72(17) |
| F(1)-C(5)-C(4)-C(3)     | 179.30(17)  |
| C(6)-C(5)-C(4)-C(3)     | -0.8(3)     |
| C(2)-C(3)-C(4)-C(5)     | 0.4(3)      |
| C(20)-C(15)-C(16)-C(17) | 2.2(3)      |
| C(8)-C(15)-C(16)-C(17)  | 179.02(18)  |
| C(15)-C(20)-C(19)-C(18) | -0.6(3)     |
| C(15)-C(16)-C(17)-C(18) | -1.2(3)     |
| C(20)-C(19)-C(18)-C(17) | 1.6(3)      |
| C(16)-C(17)-C(18)-C(19) | -0.7(4)     |
| C(13)-C(12)-C(11)-C(10) | -0.2(3)     |
| C(9)-C(10)-C(11)-C(12)  | -0.6(3)     |
| C(11)-C(12)-C(13)-C(14) | 1.2(3)      |
| C(9)-C(14)-C(13)-C(12)  | -1.5(3)     |

---

---

Symmetry transformations used to generate equivalent atoms: