

Electronic supplementary information

**Four-component radical-dual-difunctionalization (RDD) and  
decarbonylative alkylative peroxidation of two different alkenes with  
aliphatic aldehydes and TBHP**

Ren-Xiang Liu, Feng Zhang, Yong Peng and Luo Yang\*

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## I. General information

Unless otherwise noted, all commercially available compounds were used as provided without further purification. Dry solvents (toluene, ethyl acetate, dichloroethane, acetonitrile, chlorobenzene, fluorobenzene) were used as commercially available. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm) or Sorbent Silica Gel 60 F254 plates. The developed chromatography was analyzed by UV lamp (254 nm). Unless other noted, High-resolution mass spectra (HRMS) were obtained from a JEOL JMS-700 instrument (ESI). Melting points are uncorrected. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature. Chemical shifts for  $^1\text{H}$  NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent resonance as the internal standard (chloroform:  $\delta$  7.26 ppm). Chemical shifts for  $^{13}\text{C}$  NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent as the internal standard ( $\text{CDCl}_3$ :  $\delta$  77.16 ppm). Data are reported as following: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet, br = broad signal), coupling constant (Hz), and integration.

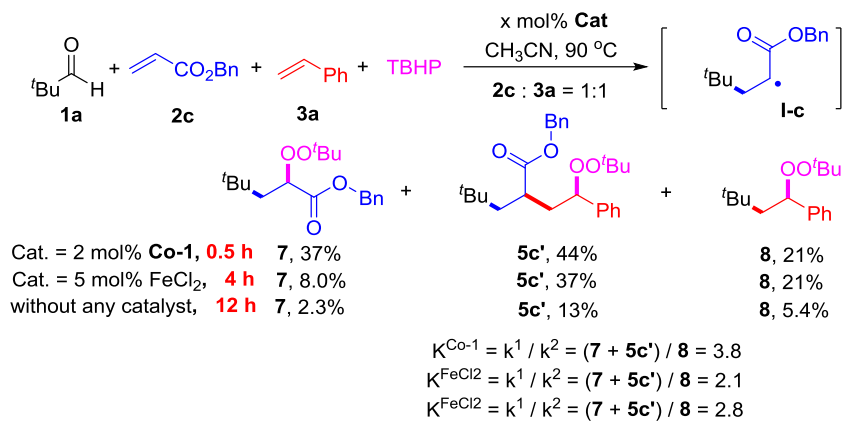
The d.r. were determined by the GC of reaction mixtures by assuming the diastereo-isomers with the same responses under the FID detector.

## II. General experimental procedures

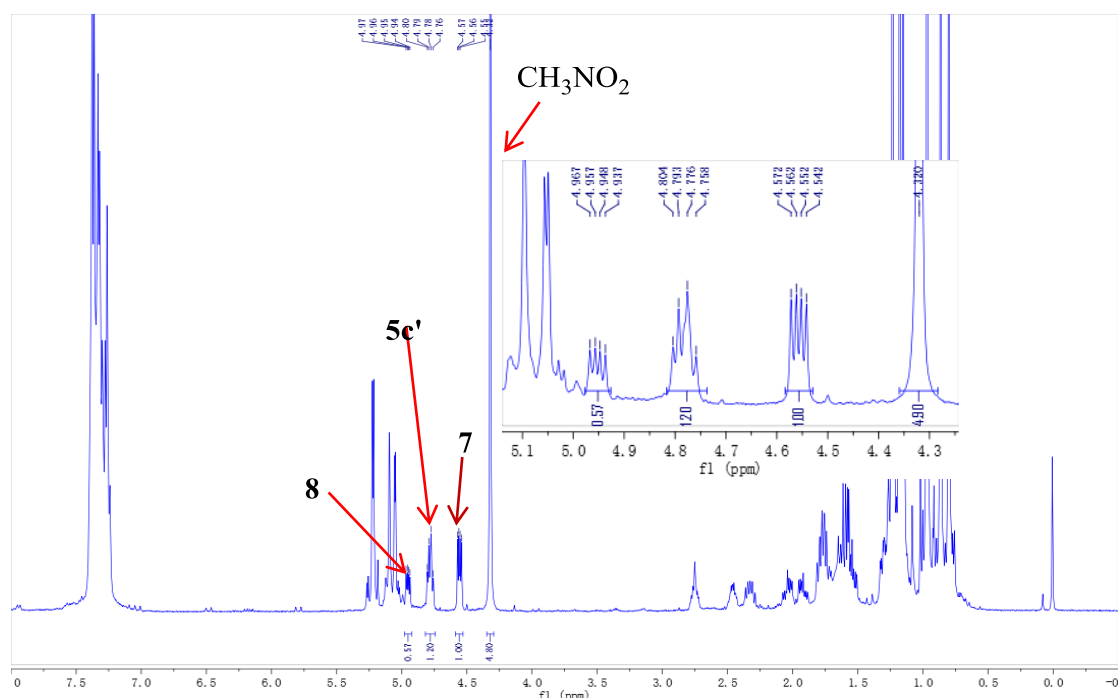
An oven-dried microwave reaction vessel was successively charged with salen-Co complex (**Co-1**, 2.0 mol%) in  $\text{CH}_3\text{CN}$  (1 mL, pre-prepared solution), pivaldehyde (**1a**, 0.8 mmol, 4.0 equiv), methyl acrylate (**2a**, 0.2 mmol, 1.0 equiv), styrene (**3a**, 0.4 mmol, 2.0 equiv) and *tert*-butyl hydroperoxide (TBHP, 70% in water, 1.0 mmol, 5.0 equiv). The vessel was sealed and heated at 90 °C (oil bath temperature) for 12 h. Afterwards the resulting mixture was cooled to room temperature, DBU (0.3 mmol, 1.5 equiv) was added and the mixture was heated for another 8 hours at 70 °C. Then the resulting mixture was cooled to room temperature again, and the solvent was removed in vacuum. The residue was purified by column chromatography on silica gel with a mixture of ethyl acetate/petroleum ether (30:1,  $R_f$  = 0.4) as eluent to give products **4a**.

## III. The relative reaction rate of two different alkenes

1) In order to explore the relative reaction rate of alkyl radical with the two alkenes, we added *equal amounts* of two different olefins and shorten the reaction time to *0.5 hour*. The details are as follows: an oven-dried microwave reaction vessel was charged with salen-Co complex (**Co-1**, 2.0 mol%) in  $\text{CH}_3\text{CN}$  (1 mL, pre-prepared solution), pivaldehyde (**1a**, 0.8 mmol, 4.0 equiv), benzyl acrylate (**2c**, 0.2 mmol, 1.0 equiv), styrene (**3a**, 0.2 mmol, 1.0 equiv) and *tert*-butyl hydroperoxide (TBHP, 70% in water, 1.0 mmol, 5.0 equiv). The vessel was sealed and heated at 90 °C (oil bath temperature) for *0.5 h*. Then, we carefully isolated the reaction mixture by column chromatography and preparative TLC, three main-products (**7**, **5c'** and **8**) were obtained and characterized. Their yields were determined by the  $^1\text{H}$  NMR of reaction mixture using  $\text{CH}_3\text{NO}_2$  (7.3 mg) as the internal standard.

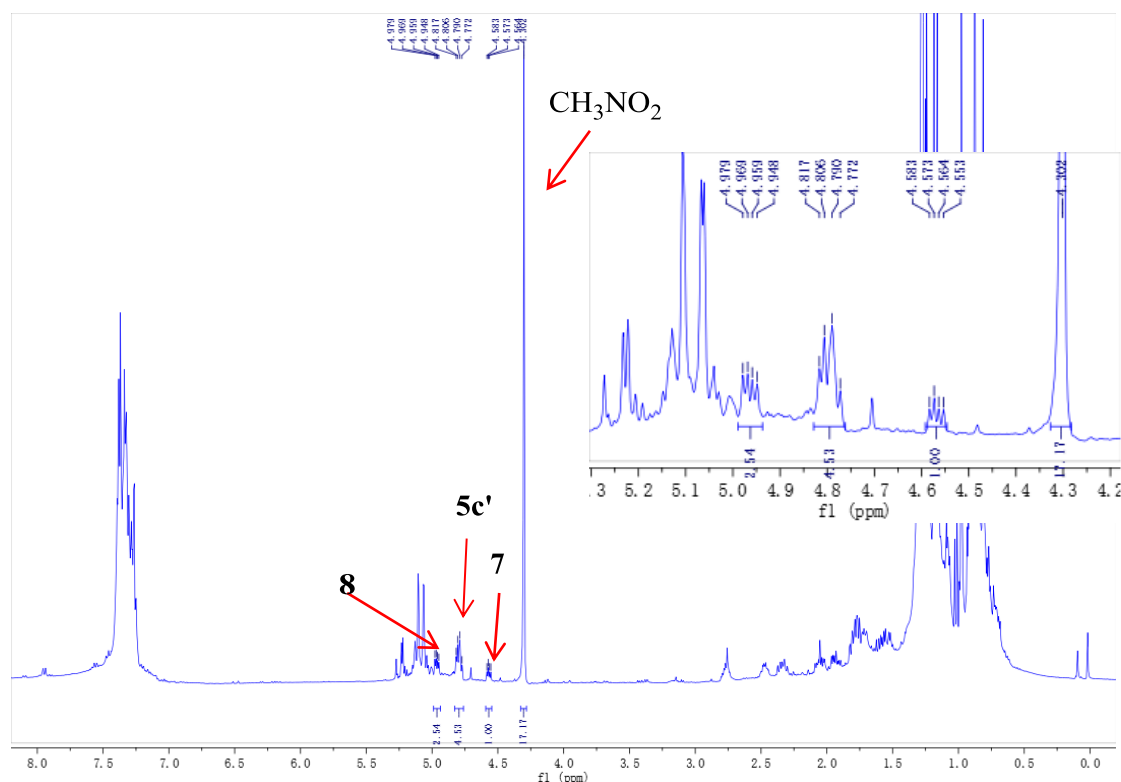


**2 mol% Co-1, 0.5 h** (crude NMR)



2) As a control, the Fe-promoted RDD was performed as follows: an oven-dried microwave reaction vessel was charged with FeCl<sub>2</sub> (**5.0 mol%**) in CH<sub>3</sub>CN (1 mL), pivaldehyde (**1a**, 0.8 mmol, 4.0 equiv), benzyl acrylate (**2c**, 0.2 mmol, 1.0 equiv), styrene (**3a**, 0.2 mmol, 1.0 equiv) and *tert*-butyl hydroperoxide (TBHP, 70% in water, 1.0 mmol, 5.0 equiv). The vessel was sealed and heated at 90 °C (oil bath temperature) for **4 h**. Then, we carefully isolated the reaction mixture, three main-products (**7**, **5c'** and **8**) were obtained and characterized. Their yields were determined by the <sup>1</sup>H NMR of reaction mixture using CH<sub>3</sub>NO<sub>2</sub> (5.8 mg) as the internal standard.

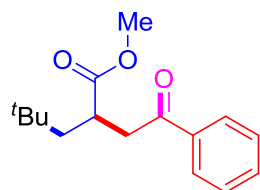
**5 mol% FeCl<sub>2</sub>, 4 h** (crude NMR)



3) For the reaction proceeded without any metal-catalyst: an oven-dried microwave reaction vessel was charged with  $\text{CH}_3\text{CN}$  (1 mL), pivaldehyde (**1a**, 0.8 mmol, 4.0 equiv), benzyl acrylate (**2c**, 0.2 mmol, 1.0 equiv), styrene (**3a**, 0.2 mmol, 1.0 equiv) and *tert*-butyl hydroperoxide (TBHP, 70% in water, 1.0 mmol, 5.0 equiv). The vessel was sealed and heated at 90 °C (oil bath temperature) for 12 h. Then, we carefully isolated the reaction mixture by column chromatography and preparative TLC, three main-products (**7**, **5c'** and **8**) were obtained and characterized. Their yields were determined by the  $^1\text{H}$  NMR of reaction mixture using  $\text{CH}_3\text{NO}_2$  as the internal standard.

#### IV. Spectra data of products **4a-4l**, **5b-5k**, **6b-6g**, **7**, **8**, **5c'**, **9b**, **9i**, **10**.

##### (4a) methyl 4,4-dimethyl-2-(2-oxo-2-phenylethyl)pentanoate <sup>4</sup>

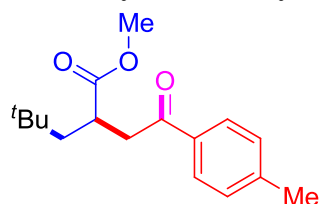


The title compound was prepared according to the general procedure described above by the reaction between styrene (**3a**), pivaldehyde (**1a**), methyl acrylate (**2a**), with TBHP and DBU, and purified by flash column chromatography as colorless oil (32.5 mg, 62%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (d,  $J = 8.0$  Hz, 2H), 7.57 (t,  $J = 8.0$  Hz, 1H), 7.46 (t,  $J = 8.0$  Hz, 2H), 3.69 (s, 3H), 3.42 – 3.35 (m, 1H), 3.14 – 3.07 (m, 2H), 1.79 (dd,  $J = 14.0, 8.0$  Hz, 1H), 1.36 (dd,  $J = 14.0, 3.6$  Hz, 1H), 0.93 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  198.06, 177.29, 136.69,

133.33, 128.71, 128.12, 51.93, 46.15, 43.17, 37.16, 31.06, 29.47. IR (cm<sup>-1</sup>): 2953, 2868, 1733, 1684, 1597, 757, 691.

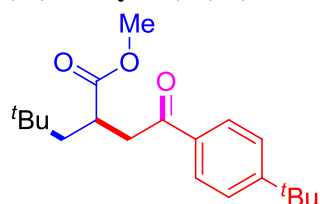
**(4b) methyl 4,4-dimethyl-2-(2-oxo-2-(*p*-tolyl)ethyl)pentanoate**



The title compound was prepared according to the general procedure described above by the reaction between 1-methyl-4-vinylbenzene (**3b**), pivaldehyde (**1a**), methyl acrylate (**2a**), with TBHP and DBU, and purified by flash column chromatography as colorless oil (37.0 mg, 67%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.84 (d,  $J$  = 8.0 Hz, 2H), 7.25 (d,  $J$  = 8.0 Hz, 2H), 3.68 (s, 3H), 3.38 – 3.31 (m, 1H), 3.13 – 3.04 (m, 2H), 2.41 (s, 3H), 1.78 (dd,  $J$  = 14.0, 8.0 Hz, 1H), 1.35 (dd,  $J$  = 14.0, 3.6 Hz, 1H), 0.93 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  197.72, 177.41, 144.16, 134.31, 129.42, 128.29, 51.94, 46.21, 43.09, 37.27, 31.10, 29.51, 21.78. IR (cm<sup>-1</sup>): 2952, 2868, 1735, 1685, 1607, 968, 810. HRMS: calcd. for C<sub>17</sub>H<sub>24</sub>O<sub>3</sub>Na<sup>+</sup> [M+ Na]<sup>+</sup>: 299.1618; Found: 299.1595.

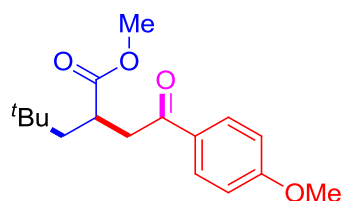
**(4c) methyl 2-(2-(4-(*tert*-butyl)phenyl)-2-oxoethyl)-4,4-dimethylpentanoate**



The title compound was prepared according to the general procedure described above by the reaction between 1-(*tert*-butyl)-4-vinylbenzene (**3c**), pivaldehyde (**1a**), methyl acrylate (**2a**), with TBHP and DBU, and purified by flash column chromatography as colorless oil (44.6 mg, 70%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.90 (d,  $J$  = 8.0 Hz, 2H), 7.48 (d,  $J$  = 8.0 Hz, 2H), 3.69 (s, 3H), 3.39 – 3.32 (m, 1H), 3.15 – 3.06 (m, 2H), 1.79 (dd,  $J$  = 12.0, 8.0 Hz, 1H), 1.39 – 1.33 (m, 10H), 0.94 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  197.74, 177.43, 157.12, 134.19, 128.14, 125.69, 51.96, 46.19, 43.09, 37.22, 35.26, 31.21, 31.10, 29.51. IR (cm<sup>-1</sup>): 2956, 2869, 1733, 1683, 1606, 970, 826. HRMS: calcd. for C<sub>20</sub>H<sub>30</sub>O<sub>3</sub>Na<sup>+</sup> [M+ Na]<sup>+</sup>: 341.2087; Found: 341.2071.

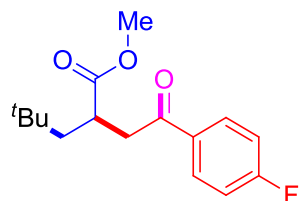
**(4d) methyl 2-(2-(4-methoxyphenyl)-2-oxoethyl)-4,4-dimethylpentanoate**



The title compound was prepared according to the general procedure described above by the reaction between 1-methoxy-4-vinylbenzene (**3d**), pivaldehyde (**1a**), methyl acrylate (**2a**), with TBHP and DBU, and purified by flash column chromatography as colorless oil (36.2 mg, 62%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.93 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H), 3.68 (s, 3H), 3.32 (m, 1H), 3.16 – 2.99 (m, 2H), 1.78 (dd, *J* = 14.0, 8.0 Hz, 1H), 1.35 (dd, *J* = 14.0, 3.2 Hz, 1H), 0.93 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  196.58, 177.42, 163.72, 130.44, 129.93, 113.88, 55.59, 51.89, 46.22, 42.85, 37.38, 31.08, 29.51. IR (cm<sup>-1</sup>): 2953, 2868, 1732, 1681, 1601, 830. HRMS: calcd. for C<sub>17</sub>H<sub>24</sub>O<sub>4</sub>Na<sup>+</sup> [M+ Na]<sup>+</sup>: 315.1567; Found: 315.1555.

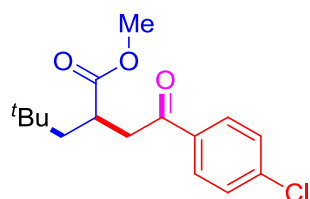
**(4e) methyl 2-(2-(4-fluorophenyl)-2-oxoethyl)-4,4-dimethylpentanoate**



The title compound was prepared according to the general procedure described above by the reaction between 1-fluoro-4-vinylbenzene (**3e**), pivaldehyde (**1a**), methyl acrylate (**2a**), with TBHP and DBU, and purified by flash column chromatography as colorless oil (35.9 mg, 64%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.06 – 7.89 (m, 2H), 7.13 (t, *J* = 8.8 Hz, 1H), 3.69 (s, 2H), 3.40 – 3.33 (m, 1H), 3.13 – 3.03 (m, 2H), 1.78 (dd, *J* = 14.0, 8.0 Hz, 1H), 1.35 (dd, *J* = 14.0, 3.6 Hz, 1H), 0.94 (s, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  196.53, 177.27, 165.94 (d, *J* = 253.3 Hz), 133.11, 130.80 (d, *J* = 9.3 Hz), 115.85 (d, *J* = 21.8 Hz), 52.00, 46.18, 43.09, 37.16, 31.10, 29.48. IR (cm<sup>-1</sup>): 2954, 2869, 1736, 1688, 1597, 969, 831. HRMS: calcd. for C<sub>16</sub>H<sub>21</sub>FO<sub>3</sub>Na<sup>+</sup> [M+ Na]<sup>+</sup>: 303.1367; Found: 303.1367.

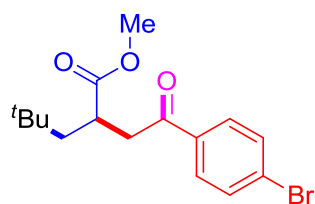
**(4f) methyl 2-(2-(4-chlorophenyl)-2-oxoethyl)-4,4-dimethylpentanoate**



The title compound was prepared according to the general procedure described above by the reaction between 1-chloro-4-vinylbenzene (**3f**), pivaldehyde (**1a**), methyl acrylate (**2a**), with TBHP and DBU, and purified by flash column chromatography as colorless oil (34.4 mg, 58%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.89 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 2H), 3.69 (s, 3H), 3.39 – 3.33 (m, 1H), 3.12 – 3.02 (m, 2H), 1.78 (dd, *J* = 14.0, 8.0 Hz, 1H), 1.35 (dd, *J* = 14.0, 4.0 Hz, 1H), 0.93 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  196.93, 177.22, 139.83, 134.99, 129.58, 129.07, 52.03, 46.17, 43.14, 37.13, 31.11, 29.49. IR (cm<sup>-1</sup>): 2954, 2868, 1732, 1689, 1589, 970, 821. HRMS: calcd. for C<sub>16</sub>H<sub>21</sub>ClO<sub>3</sub>Na<sup>+</sup> [M+ Na]<sup>+</sup>: 319.1071; Found: 319.1071.

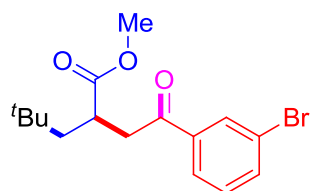
**(4g) methyl 2-(2-(4-bromophenyl)-2-oxoethyl)-4,4-dimethylpentanoate**



The title compound was prepared according to the general procedure described above by the reaction between 1-bromo-4-vinylbenzene (**3g**), pivaldehyde (**1a**), methyl acrylate (**2a**), with TBHP and DBU, and purified by flash column chromatography as colorless oil (42.8 mg, 63%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 (d,  $J = 8.4$  Hz, 2H), 7.60 (d,  $J = 8.4$  Hz, 2H), 3.68 (s, 3H), 3.38 – 3.32 (m, 1H), 3.12 – 3.01 (m, 2H), 1.78 (dd,  $J = 14.0, 8.0$  Hz, 1H), 1.35 (dd,  $J = 14.0, 3.6$  Hz, 1H), 0.93 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  197.16, 177.23, 135.39, 132.08, 129.69, 128.59, 52.05, 46.18, 43.13, 37.13, 31.12, 29.50. IR ( $\text{cm}^{-1}$ ): 2953, 2868, 1735, 1688, 1585, 969, 816. HRMS: calcd. for  $\text{C}_{16}\text{H}_{21}\text{BrO}_3\text{Na}^+$   $[\text{M} + \text{Na}]^+$ : 363.0566; Found: 363.0562.

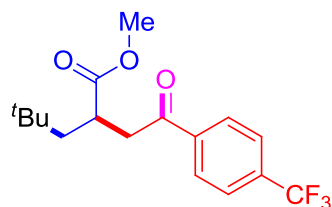
**(4h) methyl 2-(2-(3-bromophenyl)-2-oxoethyl)-4,4-dimethylpentanoate**



The title compound was prepared according to the general procedure described above by the reaction between 1-bromo-3-vinylbenzene (**3h**), pivaldehyde (**1a**), methyl acrylate (**2a**), with TBHP and DBU, and purified by flash column chromatography as colorless oil (37.4 mg, 55%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 (s, 1H), 7.67 (d,  $J = 8.0$  Hz, 1H), 7.69 (dd,  $J = 8.0, 0.8$  Hz, 1H), 7.35 (t,  $J = 8.0$  Hz, 1H), 3.69 (s, 3H), 3.39 – 3.33 (m, 1H), 3.13 – 3.02 (m, 2H), 1.78 (dd,  $J = 14.0, 8.0$  Hz, 1H), 1.35 (dd,  $J = 14.0, 8.0$  Hz, 1H), 0.94 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.78, 177.13, 138.37, 136.21, 131.25, 130.36, 126.67, 123.11, 52.04, 46.15, 43.22, 37.06, 31.11, 29.49. IR ( $\text{cm}^{-1}$ ): 2953, 2868, 1735, 1692, 1567, 870, 787. HRMS: calcd. for  $\text{C}_{16}\text{H}_{21}\text{BrO}_3^+$   $[\text{M} + \text{Na}]^+$ : 363.0566; Found: 363.0549.

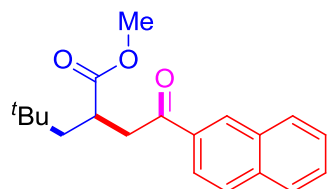
**(4i) methyl 4,4-dimethyl-2-(2-oxo-2-(4-(trifluoromethyl)phenyl)ethyl)pentanoate**



The title compound was prepared according to the general procedure described above by the reaction between 1-(trifluoromethyl)-4-vinylbenzene (**3i**), pivaldehyde (**1a**), methyl acrylate (**2a**), with TBHP and DBU, and purified by flash column chromatography as colorless oil (27.1 mg, 41%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 (d,  $J = 8.0$  Hz, 2H), 7.73 (d,  $J = 8.4$  Hz, 2H), 3.44 – 3.39 (m, 1H), 3.15 – 3.07 (m, 2H), 1.80 (dd,  $J = 14.0, 8.0$  Hz, 1H), 1.36 (dd,  $J = 14.0, 3.6$  Hz, 1H), 0.94 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  197.25, 177.09, 139.33, 134.66 (q,  $J = 32.5$  Hz), 128.51, 125.84 (q,  $J = 3.7$  Hz), 123.68 (d,  $J = 271.2$  Hz), 52.06, 46.17, 43.42, 37.11, 31.13, 29.48. IR ( $\text{cm}^{-1}$ ): 2955, 2871, 1732, 1694, 1582, 970, 830. HRMS: calcd. for  $\text{C}_{17}\text{H}_{21}\text{F}_3\text{O}_3\text{Na}^+$  [ $\text{M} + \text{Na}$ ] $^+$ : 353.1335; Found: 353.1332.

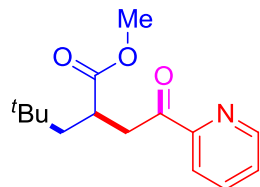
**(4j) methyl 4,4-dimethyl-2-(2-(naphthalen-2-yl)-2-oxoethyl)pentanoate**



The title compound was prepared according to the general procedure described above by the reaction between 2-vinylnaphthalene (**3j**), pivaldehyde (**1a**), methyl acrylate (**2a**), with TBHP and DBU, and purified by flash column chromatography as colorless oil (40.0 mg, 64%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.48 (s, 1H), 8.02 (dd,  $J = 8.6, 1.6$  Hz, 1H), 7.97 (d,  $J = 7.9$  Hz, 1H), 7.92 – 7.86 (m, 2H), 7.64 – 7.54 (m, 2H), 3.71 (s, 3H), 3.56 – 3.50 (m, 1H), 3.28 – 3.15 (m, 2H), 1.84 (dd,  $J = 14.0, 8.0$  Hz, 1H), 1.42 (dd,  $J = 14.0, 3.6$  Hz, 1H), 0.96 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  198.04, 177.43, 135.75, 134.05, 132.59, 129.92, 129.71, 128.67, 128.62, 127.91, 126.95, 123.85, 52.01, 46.25, 43.25, 37.31, 31.13, 29.52. IR ( $\text{cm}^{-1}$ ): 3059, 2952, 2868, 1736, 1682, 1596, 822, 749. HRMS: calcd. for  $\text{C}_{20}\text{H}_{24}\text{O}_3\text{Na}^+$  [ $\text{M} + \text{Na}$ ] $^+$ : 335.1618; Found: 335.1614.

**(4k) methyl 4,4-dimethyl-2-(2-oxo-2-(pyridin-2-yl)ethyl)pentanoate**

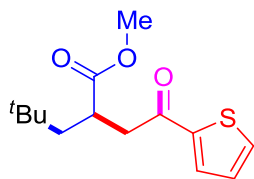


The title compound was prepared according to the general procedure described above by the reaction between 2-vinylpyridine (**3k**), pivaldehyde (**1a**), methyl acrylate (**2a**), with TBHP and DBU, and purified by flash column chromatography as colorless oil (24.2 mg, 46%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.68 (d,  $J = 4.0$  Hz, 1H), 8.02 (d,  $J = 7.8$  Hz, 1H), 7.83 (td,  $J = 7.6, 1.6$  Hz, 1H), 7.51 – 7.44 (m, 1H), 3.68 (s, 3H), 3.62 – 3.55 (m, 1H), 3.47 – 3.41 (m, 1H), 3.11 – 3.05 (m, 1H), 1.82 (dd,  $J = 14.0, 8.0$  Hz, 1H), 1.40 (dd,  $J = 14.0, 4.0$  Hz, 1H), 0.94 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  199.89, 177.32, 153.22, 149.10, 137.04, 127.39, 121.92, 51.89, 46.13, 42.58, 37.14, 31.12, 29.52. IR ( $\text{cm}^{-1}$ ): 2954, 2868, 1736, 1701, 970, 777. HRMS: calcd. for  $\text{C}_{15}\text{H}_{21}\text{NO}_3\text{Na}^+$  [ $\text{M} + \text{Na}$ ] $^+$ : 286.1414; Found: 286.1407.

**(4l) methyl 4,4-dimethyl-2-(2-oxo-2-(thiophen-2-yl)ethyl)pentanoate**

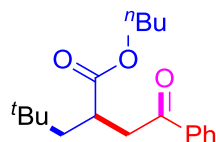




The title compound was prepared according to the general procedure described above by the reaction between 2-vinylthiophene (**3l**), pivaldehyde (**1a**), methyl acrylate (**2a**), with TBHP and DBU, and purified by flash column chromatography as colorless oil (18.2 mg, 34%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72 (d,  $J = 3.6$  Hz, 1H), 7.64 (d,  $J = 4.8$  Hz, 1H), 7.13 (t,  $J = 4.4$  Hz, 1H), 3.68 (s, 3H), 3.32 - 3.27 (m, 1H), 3.15 - 2.99 (m, 2H), 1.80 (dd,  $J = 14.0, 8.0$  Hz, 1H), 1.35 (dd,  $J = 14.0, 3.6$  Hz, 1H), 0.92 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  190.91, 177.10, 143.97, 133.94, 132.15, 128.25, 52.00, 46.07, 43.66, 37.38, 31.07, 29.47. IR ( $\text{cm}^{-1}$ ): 3093, 2953, 2868, 1732, 1668, 933, 724. HRMS: calcd. for  $\text{C}_{14}\text{H}_{20}\text{SO}_3\text{Na}^+$   $[\text{M} + \text{Na}]^+$ : 291.1025; Found: 291.1022.

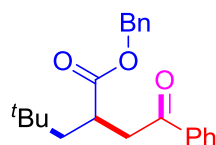
**(5b) butyl 4,4-dimethyl-2-(2-oxo-2-phenylethyl)pentanoate**



The title compound was prepared according to the general procedure described above by the reaction between styrene (**3a**), pivaldehyde (**1a**), butyl acrylate (**2b**), with TBHP and DBU, and purified by flash column chromatography as colorless oil (38.3 mg, 63%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (d,  $J = 7.6$  Hz, 2H), 7.56 (t,  $J = 7.6$  Hz, 1H), 7.46 (t,  $J = 7.6$  Hz, 2H), 4.07 (t,  $J = 6.4$  Hz, 2H), 3.41 - 3.34 (m, 1H), 3.13 - 3.05 (m, 2H), 1.80 (dd,  $J = 14.0, 7.6$  Hz, 1H), 1.66 - 1.58 (m, 2H), 1.42 - 1.32 (m, 3H), 0.94 - 0.90 (m, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  198.13, 176.87, 136.83, 133.30, 128.72, 128.16, 64.64, 46.08, 43.13, 37.43, 31.14, 30.65, 29.53, 19.30, 13.82. IR ( $\text{cm}^{-1}$ ): 2939, 2868, 1730, 1682, 1598, 756, 690. HRMS: calcd. for  $\text{C}_{19}\text{H}_{28}\text{O}_3\text{Na}^+$   $[\text{M} + \text{Na}]^+$ : 327.1931; Found: 327.1931.

**(5c) benzyl 4,4-dimethyl-2-(2-oxo-2-phenylethyl)pentanoate**

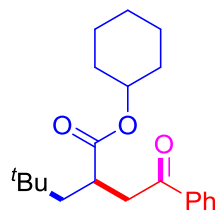


The title compound was prepared according to the general procedure described above by the reaction between styrene (**3a**), pivaldehyde (**1a**), benzyl acrylate (**2c**), with TBHP and DBU, and purified by flash column chromatography as colorless oil (40.6 mg, 60%)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 - 7.92 (m, 2H), 7.56 (t,  $J = 7.6$  Hz, 1H), 7.45 (t,  $J = 7.6$  Hz, 2H), 7.35 - 7.29 (m, 5H), 5.11 (s, 2H), 3.40 - 3.34 (m, 1H), 3.19 - 3.01 (m, 2H), 1.81 (dd,  $J = 14.0,$

7.6 Hz, 1H), 1.35 (dd,  $J = 14.0, 3.6$  Hz, 1H), 0.92 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  197.99, 176.56, 136.79, 136.03, 133.34, 128.74, 128.59, 128.35, 128.22, 128.18, 66.63, 45.99, 43.06, 37.39, 31.15, 29.54. IR ( $\text{cm}^{-1}$ ): 3088, 3064, 3033, 2955, 1732, 1683, 1597, 752, 693. HRMS: calcd. for  $\text{C}_{22}\text{H}_{26}\text{O}_3\text{Na}^+$   $[\text{M} + \text{Na}]^+$ : 361.1774; Found: 361.1774.

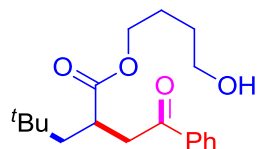
**(5d) cyclohexyl 4,4-dimethyl-2-(2-oxo-2-phenylethyl)pentanoate**



The title compound was prepared according to the general procedure described above by the reaction between styrene (**3a**), pivaldehyde (**1a**), cyclohexyl acrylate (**2d**), with TBHP and DBU, and purified by flash column chromatography as colorless oil (42.3 mg, 64%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (d,  $J = 7.6$  Hz, 2H), 7.56 (t,  $J = 7.6$  Hz, 1H), 7.46 (t,  $J = 7.6$  Hz, 2H), 4.82 – 4.68 (m, 1H), 3.29 – 3.31 (m, 1H), 3.09 – 3.03 (m, 2H), 1.80 (dd,  $J = 14.0, 7.6$  Hz, 3H), 1.71 – 1.70 (m, 2H), 1.39 – 1.30 (m, 7H), 0.94 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  198.18, 176.15, 136.93, 133.25, 128.72, 128.17, 72.72, 46.03, 43.20, 37.73, 31.59, 31.45, 31.19, 29.59, 25.54, 23.83. IR ( $\text{cm}^{-1}$ ): 2939, 2861, 1728, 1689, 1581, 757, 690. HRMS: calcd. for  $\text{C}_{21}\text{H}_{30}\text{O}_3\text{Na}^+$   $[\text{M} + \text{Na}]^+$ : 353.2087; Found: 353.2087.

**(5e) 4-hydroxybutyl 4,4-dimethyl-2-(2-oxo-2-phenylethyl)pentanoate**



The title compound was prepared according to the general procedure described above by the reaction between styrene (**3a**), pivaldehyde (**1a**), 4-hydroxybutyl acrylate (**2e**), with TBHP and DBU, and purified by flash column chromatography as colorless oil (34.6 mg, 54%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 – 7.93 (m, 2H), 7.57 (t,  $J = 7.6$  Hz, 1H), 7.46 (t,  $J = 7.6$  Hz, 2H), 4.19 – 4.09 (m, 1H), 4.07 – 4.03 (m, 1H), 3.68 – 3.65 (m, 2H), 3.39 (q,  $J = 9.6$  Hz, 1H), 3.12 – 3.05 (m, 2H), 1.80 – 1.62 (m, 6H), 1.36 (dd,  $J = 14.0, 3.6$  Hz, 1H), 0.94 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  198.30, 176.86, 136.71, 133.38, 128.74, 128.15, 64.57, 62.43, 46.13, 43.22, 37.39, 31.14, 29.54, 29.31, 25.07. IR ( $\text{cm}^{-1}$ ): 3062, 2954, 1732, 1683, 1597, 1040, 756, 690. HRMS: calcd. for  $\text{C}_{19}\text{H}_{28}\text{O}_4\text{Na}^+$   $[\text{M} + \text{Na}]^+$ : 343.1880; Found: 343.1863.

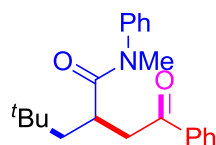
**(5f) *N,N*,4,4-tetramethyl-2-(2-oxo-2-phenylethyl)pentanamide**



The title compound was prepared according to the general procedure described above by the reaction between styrene (**3a**), pivaldehyde (**1a**), *N,N*-dimethylacrylamide (**2f**), with TBHP and DBU, and purified by flash column chromatography as colorless oil (35.8 mg, 65%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (d,  $J = 7.6$  Hz, 2H), 7.55 (t,  $J = 7.6$  Hz, 1H), 7.45 (t,  $J = 7.6$  Hz, 2H), 3.49 – 3.44 (m, 2H), 3.25 (s, 3H), 3.11 - 3.04 (m, 1H), 2.93 (s, 3H), 1.88 (dd,  $J = 14.0, 7.2$  Hz, 1H), 1.33 (dd,  $J = 14.0, 4.0$  Hz, 1H), 0.93 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  199.22, 176.56, 136.87, 133.31, 128.69, 128.20, 46.84, 44.01, 37.77, 36.12, 32.87, 31.11, 29.97. IR ( $\text{cm}^{-1}$ ): 2954, 2869, 1683, 1646, 1597, 741, 691. HRMS: calcd. for  $\text{C}_{17}\text{H}_{25}\text{NO}_2\text{Na}^+$  [ $\text{M} + \text{Na}$ ] $^+$ : 298.1778; Found: 298.1775.

**(5g) *N*,4,4-trimethyl-2-(2-oxo-2-phenylethyl)-*N*-phenylpentanamide**



The title compound was prepared according to the general procedure described above by the reaction between styrene (**3a**), pivaldehyde (**1a**), *N*-methyl-*N*-phenylacrylamide (**2g**), with TBHP and DBU, and purified by flash column chromatography as colorless oil (40.5 mg, 60%)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 (d,  $J = 7.2$  Hz, 2H), 7.55 (t,  $J = 7.2$  Hz, 1H), 7.47 – 7.40 (m, 6H), 7.37 – 7.32 (m, 1H), 3.50 - 3.44 (m, 1H), 3.28 (s, 3H), 3.24 – 3.22 (m, 1H), 3.17 – 3.11 (m, 1H), 1.70 – 1.64 (m, 1H), 1.28 (dd,  $J = 14.0, 6.7$  Hz, 1H), 0.67 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  198.94, 176.26, 144.00, 137.00, 133.18, 129.81, 128.66, 128.18, 127.88, 127.86, 45.74, 42.69, 37.97, 34.47, 31.00, 29.82. IR ( $\text{cm}^{-1}$ ): 3061, 2956, 2867, 1685, 1653, 1596, 734, 701. HRMS: calcd. for  $\text{C}_{22}\text{H}_{27}\text{NO}_2\text{Na}^+$  [ $\text{M} + \text{Na}$ ] $^+$ : 360.1934; Found: 360.1932.

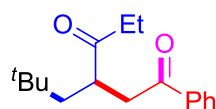
**(5h) 4,4-dimethyl-2-(2-oxo-2-phenylethyl)pentanenitrile** <sup>4</sup>



The title compound was prepared according to the general procedure described above by the reaction between styrene (**3a**), pivaldehyde (**1a**), acryloyl cyanide (**2h**), with TBHP and DBU, and purified by flash column chromatography as white solid (22.0 mg, 49%).

M.p. 83-85 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (d,  $J = 7.6$  Hz, 2H), 7.61 (t,  $J = 7.6$  Hz, 1H), 7.50 (t,  $J = 7.6$  Hz, 2H), 3.46 – 3.38 (m, 1H), 3.33 – 3.22 (m, 2H), 1.76 (dd,  $J = 14.0, 10.4$  Hz, 1H), 1.41 (dd,  $J = 14.0, 2.0$  Hz, 1H), 1.06 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.34, 136.06, 133.97, 128.99, 128.16, 123.44, 46.18, 42.73, 31.17, 29.49, 22.05. IR ( $\text{cm}^{-1}$ ): 2958, 2870, 2237, 1686, 1597, 760, 692.

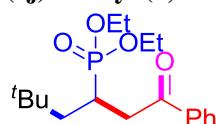
**(5i) 3-neopentyl-1-phenylhexane-1,4-dione**



The title compound was prepared according to the general procedure described above by the reaction between styrene (**3a**), pivaldehyde (**1a**), pent-1-en-3-one (**2i**), with TBHP and DBU, and purified by flash column chromatography as colorless oil (22.4 mg, 43%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 – 7.92 (m, 2H), 7.57 (t,  $J = 7.6$  Hz, 1H), 7.46 (t,  $J = 7.6$  Hz, 2H), 3.55 – 3.49 (m, 1H), 3.27 – 3.21 (m, 1H), 3.05 (dd,  $J = 17.6, 4.0$  Hz, 1H), 2.79 – 2.64 (m, 2H), 1.62 – 1.58 (m, 1H), 1.28 (dd,  $J = 14.4, 6.0$  Hz, 1H), 1.09 (t,  $J = 7.2$  Hz, 3H), 0.96 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  214.33, 198.98, 136.77, 133.33, 128.72, 128.16, 44.90, 42.85, 42.76, 35.37, 31.43, 29.84, 7.95. IR ( $\text{cm}^{-1}$ ): 3063, 2957, 2869, 1714, 1686, 749, 690. HRMS: calcd. for  $\text{C}_{17}\text{H}_{24}\text{O}_2\text{Na}^+$  [ $\text{M} + \text{Na}$ ] $^+$ : 283.1669; Found: 283.1668.

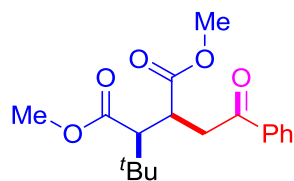
**(5j) diethyl (5,5-dimethyl-1-oxo-1-phenylhexan-3-yl)phosphonate**



The title compound was prepared according to the general procedure described above by the reaction between styrene (**3a**), pivaldehyde (**1a**), diethyl vinylphosphonate (**2j**), with TBHP and DBU, and purified by flash column chromatography as colorless oil (24.5 mg, 36%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 – 7.96 (m, 2H), 7.57 (t,  $J = 7.6$  Hz, 1H), 7.47 (t,  $J = 7.6$  Hz, 2H), 4.10 – 3.98 (m, 4H), 3.76 – 3.64 (m, 1H), 2.93 – 2.79 (m, 2H), 1.95 – 1.86 (m, 1H), 1.39 – 1.32 (m, 1H), 1.25 – 1.18 (m, 6H), 0.94 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  197.49, 136.94, 133.29, 128.76, 128.25, 62.19, 62.13, 61.75, 61.69, 42.37, 40.56, 31.86, 31.74, 29.49, 27.55, 26.15, 16.48, 16.42. IR ( $\text{cm}^{-1}$ ): 2956, 2868, 1687, 1597, 1476, 1448, 754, 691. HRMS: calcd. for  $\text{C}_{18}\text{H}_{29}\text{O}_4\text{PNa}^+$  [ $\text{M} + \text{Na}$ ] $^+$ : 363.1696; Found: 363.1690.

**(5k) dimethyl 2-(tert-butyl)-3-(2-oxo-2-phenylethyl)succinate**<sup>4</sup>



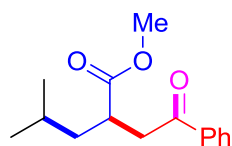
(The configuration was determined by correlation with ref 4.)

The title compound was prepared according to the general procedure described above by the reaction between styrene (**3a**), pivaldehyde (**1a**), dimethyl maleate (**2k**, dimethyl cis-butenedioate), with TBHP and DBU, and purified by flash column chromatography as colorless oil (30.1 mg, 47%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 – 7.89 (m, 2H), 7.55 (t,  $J = 7.6$  Hz, 1H), 7.46 (t,  $J = 7.6$  Hz, 2H), 3.70 (s, 3H), 3.68 (s, 3H), 3.56 – 3.42 (m, 2H), 3.16 (dd,  $J = 16.8, 1.0$  Hz, 1H), 2.79 (d,  $J = 5.6$  Hz, 1H), 1.05 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  198.04, 175.22, 173.63, 136.54, 133.43, 128.73,

128.23, 56.16, 52.35, 51.44, 39.50, 39.16, 33.77, 28.18. IR (cm<sup>-1</sup>): 2953, 2875, 1731, 1688, 1597, 1581, 760, 691.

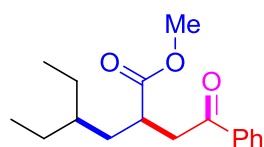
**(6b) methyl 4-methyl-2-(2-oxo-2-phenylethyl)pentanoate** <sup>4</sup>



The title compound was prepared according to the general procedure described above by the reaction between styrene (**3a**), isobutyraldehyde (**1b**), methyl acrylate (**2a**), with TBHP and DBU, and purified by flash column chromatography as colorless oil (26.3 mg, 53%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.97 – 7.95 (m, 2H), 7.57 (t,  $J$  = 7.4 Hz, 1H), 7.46 (t,  $J$  = 7.6 Hz, 2H), 3.70 (s, 3H), 3.44 (dd,  $J$  = 17.3, 8.9 Hz, 1H), 3.14 – 3.03 (m, 2H), 1.68 - 1.60 (m, 1H), 1.40 – 1.36 (m, 1H), 0.94 (dd,  $J$  = 22.8, 6.4 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  198.37, 176.60, 136.75, 133.31, 128.70, 128.15, 51.86, 41.61, 41.09, 38.64, 26.09, 22.74, 22.42. IR (cm<sup>-1</sup>): 2955, 2871, 1733, 1684, 1581, 755, 691.

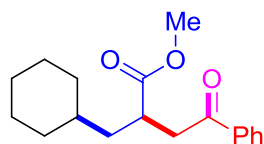
**(6c) methyl 4-ethyl-2-(2-oxo-2-phenylethyl)hexanoate**



The title compound was prepared according to the general procedure described above by the reaction between styrene (**3a**), 2-ethylbutanal (**1c**), methyl acrylate (**2a**), with TBHP and DBU, and purified by flash column chromatography as colorless oil (30.9 mg, 56%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.98 – 7.95 (m, 2H), 7.61 – 7.53 (m, 1H), 7.46 (t,  $J$  = 7.6 Hz, 2H), 3.70 (s, 3H), 3.47 – 3.40 (m, 1H), 3.15 – 3.03 (m, 2H), 1.70 – 1.63 (m, 1H), 1.47 – 1.22 (m, 6H), 0.85 (td,  $J$  = 7.2, 4.8 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  198.41, 176.68, 136.72, 133.30, 128.69, 128.14, 51.85, 41.14, 38.41, 38.13, 36.01, 25.26, 25.10, 10.62, 10.56. IR (cm<sup>-1</sup>): 2961, 2875, 1733, 1684, 1597, 756, 691. HRMS: calcd. for C<sub>17</sub>H<sub>24</sub>O<sub>3</sub>Na<sup>+</sup> [M+ Na]<sup>+</sup>: 299.1618; Found: 299.1589.

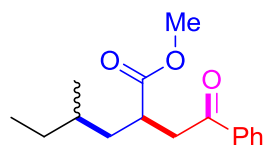
**(6d) methyl 2-(cyclohexylmethyl)-4-oxo-4-phenylbutanoate**



The title compound was prepared according to the general procedure described above by the reaction between styrene (**3a**), cyclohexanecarbaldehyde (**1d**), methyl acrylate (**2a**), with TBHP and DBU, and purified by flash column chromatography as colorless oil (26.0 mg, 45%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 – 7.95 (m, 2H), 7.57 (t,  $J = 7.6$  Hz, 1H), 7.46 (t,  $J = 7.6$  Hz, 2H), 3.70 (s, 3H), 3.46 – 3.40 (m, 1H), 3.18 – 3.02 (m, 1H), 1.84 (d,  $J = 12.8$  Hz, 1H), 1.73 – 1.59 (m, 5H), 1.43 – 1.36 (m, 1H), 1.30 – 1.12 (m, 4H), 0.95 – 0.85 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  198.43, 176.70, 136.79, 133.31, 128.71, 128.17, 51.89, 41.07, 40.06, 37.90, 35.52, 33.32, 33.25, 26.61, 26.32, 26.28. IR ( $\text{cm}^{-1}$ ): 2923, 2851, 1733, 1687, 1597, 756, 691. HRMS: calcd. for  $\text{C}_{18}\text{H}_{24}\text{O}_3\text{Na}^+$   $[\text{M} + \text{Na}]^+$ : 311.1618; Found: 311.1589.

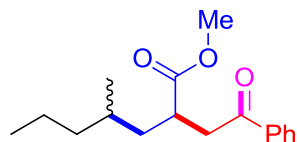
**(6e) methyl 4-methyl-2-(2-oxo-2-phenylethyl)hexanoate**



The title compound was prepared according to the general procedure described above by the reaction between styrene (**3a**), 2-methylbutanal (**1e**), methyl acrylate (**2a**), with TBHP and DBU, and purified by flash column chromatography as colorless oil (29.4 mg, 56%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 – 7.96 (m, 2H), 7.57 (t,  $J = 7.2$  Hz, 1H), 7.46 (t,  $J = 7.6$  Hz, 2H), 3.70 (s, 3H), 3.46 – 3.34 (m, 1H), 3.14 – 3.03 (m, 2H), 1.77 – 1.71 (m, 0.5 $\times$ 1H), 1.56 – 1.51 (m, 1H), 1.48 – 1.26 (m, 2.5 $\times$ 1H), 1.23 – 1.11 (m, 1H), 0.95 (d,  $J = 6.4$  Hz, 1.5 $\times$ 1H), 0.92 – 0.84 (m, 4.5 $\times$ 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  198.49, 198.37, 176.76, 176.65, 136.74, 136.71, 133.35, 128.71, 128.16, 51.94, 51.88, 41.55, 40.65, 39.70, 39.26, 38.45, 38.39, 32.44, 32.33, 29.67, 29.32, 19.09, 19.04, 11.28. IR ( $\text{cm}^{-1}$ ): 2960, 2875, 1733, 1684, 1597, 756, 691. HRMS: calcd. for  $\text{C}_{16}\text{H}_{22}\text{O}_3\text{Na}^+$   $[\text{M} + \text{Na}]^+$ : 285.1461; Found: 285.1435.

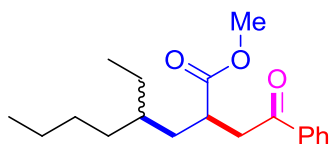
**(6f) methyl 4-methyl-2-(2-oxo-2-phenylethyl)heptanoate**



The title compound was prepared according to the general procedure described above by the reaction between styrene (**3a**), 2-methylpentanal (**1f**), methyl acrylate (**2a**), with TBHP and DBU, and purified by flash column chromatography as colorless oil (31.5 mg, 57%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 – 7.94 (m, 2H), 7.56 (t,  $J = 7.4$  Hz, 1H), 7.46 (t,  $J = 7.6$  Hz, 2H), 3.70 (s, 3H), 3.47 – 3.39 (m, 1H), 3.18 – 3.01 (m, 2H), 1.77 – 1.70 (m, 1H), 1.57 – 1.48 (m, 1.5 $\times$ 1H), 1.39 – 1.22 (m, 3.5 $\times$ 1H), 1.16 – 1.11 (m, 1H), 0.96 – 0.85 (m, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  198.48, 198.35, 176.72, 172.60, 136.74, 133.31, 128.70, 128.15, 51.88, 51.83, 41.54, 40.69, 40.06, 39.73, 39.45, 39.06, 38.49, 38.41, 30.62, 30.49, 20.00, 19.57, 19.54, 14.37. IR ( $\text{cm}^{-1}$ ): 2957, 2872, 1733, 1684, 1597, 755, 691. HRMS: calcd. for  $\text{C}_{17}\text{H}_{24}\text{O}_3\text{Na}^+$   $[\text{M} + \text{Na}]^+$ : 299.1618; Found: 299.1590.

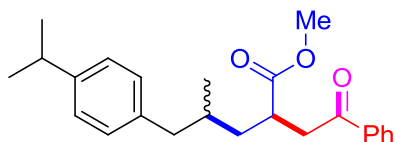
**(6g) methyl 4-ethyl-2-(2-oxo-2-phenylethyl)octanoate**



The title compound was prepared according to the general procedure described above by the reaction between styrene (**3a**), 2-ethylhexanal (**1g**), methyl acrylate (**2a**), with TBHP and DBU, and purified by flash column chromatography as colorless oil (35.3 mg, 58%).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 – 7.95 (m, 2H), 7.57 (t,  $J = 7.4$  Hz, 1H), 7.46 (t,  $J = 7.6$  Hz, 2H), 3.70 (s, 3H), 3.49 – 3.40 (m, 1H), 3.14 – 3.02 (m, 2H), 1.66 (dd,  $J = 13.2, 5.6$  Hz, 1H), 1.47 – 1.24 (m, 10H), 0.92 – 0.83 (m, 6H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  198.45, 198.41, 176.70, 176.68, 136.74, 133.31, 128.70, 128.15, 51.85, 41.23, 41.14, 38.46, 38.44, 36.74, 36.72, 36.50, 32.72, 32.55, 28.70, 28.68, 25.75, 25.61, 23.16, 14.25, 14.23, 10.56, 10.52. IR ( $\text{cm}^{-1}$ ): 2958, 2859, 1736, 1689, 1598, 755, 691. HRMS: calcd. for  $\text{C}_{19}\text{H}_{28}\text{O}_3\text{Na}^+$  [ $\text{M} + \text{Na}$ ] $^+$ : 327.1931; Found: 327.1903.

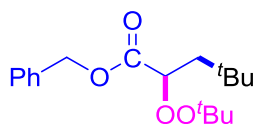
**(6h) methyl 5-(4-isopropylphenyl)-4-methyl-2-(2-oxo-2-phenylethyl)pentanoate**



The title compound was prepared according to the general procedure described above by the reaction between styrene (**3a**), 3-(4-isopropylphenyl)-2-methylpropanal (**1h**), methyl acrylate (**2a**), with TBHP and DBU, and purified by flash column chromatography as colorless oil (41.3 mg, 53%).

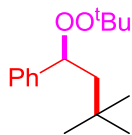
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 – 7.93 (m, 2H), 7.56 (t,  $J = 7.4$  Hz, 1H), 7.45 (t,  $J = 7.6$  Hz, 2H), 7.15 – 7.00 (m, 4H), 3.69 (d,  $J = 14.8$  Hz, 3H), 3.47 – 3.36 (m, 1H), 3.22 – 3.15 (m, 1H), 3.06 – 2.97 (m, 1H), 2.92 – 2.83 (m, 1H), 2.73 (dd,  $J = 13.6, 5.6$  Hz, 1H), 2.59 (dd,  $J = 13.2, 5.6$  Hz, 1H), 2.41 – 2.36 (m, 1H), 1.83 – 1.72 (m, 1.5 $\times$ 1H), 1.66 – 1.54 (m, 1.5 $\times$ 1H), 1.25 – 1.22 (m, 6H), 0.92 (dd,  $J = 25.6, 6.4$  Hz, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  198.40, 198.21, 176.55, 176.33, 146.49, 146.46, 138.14, 137.97, 136.71, 133.34, 129.22, 129.18, 128.72, 128.17, 126.36, 126.32, 51.95, 51.86, 43.40, 42.88, 41.61, 40.61, 39.72, 39.31, 38.46, 33.79, 33.20, 32.93, 24.18, 19.60, 19.35. IR ( $\text{cm}^{-1}$ ): 3055, 3007, 2958, 2925, 2870, 1732, 1684, 1597, 755, 691. HRMS: calcd. for  $\text{C}_{24}\text{H}_{30}\text{O}_3\text{Na}^+$  [ $\text{M} + \text{Na}$ ] $^+$ : 389.2087; Found: 389.2060.

**(7) benzyl 2-(tert-butylperoxy)-4,4-dimethylpentanoate**<sup>5</sup>



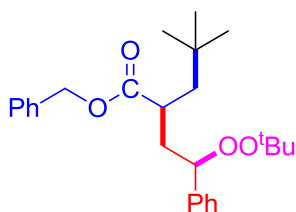
Colorless oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 – 7.31 (m, 5H), 5.25 – 5.18 (m, 2H), 4.55 (dd,  $J = 8.0, 4.4$  Hz, 1H), 1.64 – 1.53 (m, 2H), 1.23 (s, 9H), 0.96 (s, 9H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.67, 136.00, 128.58, 128.25, 128.23, 80.67, 80.61, 66.47, 44.15, 30.31, 29.92, 26.61. IR ( $\text{cm}^{-1}$ ): 2933, 2850, 1684, 1598, 1180, 756, 690.

**(8) 1-(*tert*-butylperoxy)-3,3-dimethylbutyl)benzene**<sup>5,6</sup>



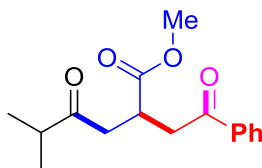
Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.36 – 7.22 (m, 5H), 4.94 (dd, *J* = 8.0, 4.4 Hz, 1H), 1.77 (dd, *J* = 14.8, 8.0 Hz, 1H), 1.52 (dd, *J* = 14.8, 4.4 Hz, 1H), 1.17 (s, 9H), 0.96 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 143.88, 128.15, 127.30, 126.99, 83.40, 79.50, 49.47, 30.49, 30.32, 26.83. IR (cm<sup>-1</sup>): 3030, 2955, 2868, 1455, 1362, 1198, 698.

**(5c) benzyl 2-(-2-(*tert*-butylperoxy)-2-phenylethyl)-4,4-dimethylpentanoate**<sup>7</sup>



Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.38 – 7.23 (m, 10H), 5.09 – 5.04 (m, 2H), 4.80 – 4.75 (m, 1H), 2.75 (ddd, *J* = 13.3, 8.8, 4.4 Hz, 1H), 2.49 – 2.42 (m, 1H), 2.35 – 2.28 (m, 1H), 2.03 (ddd, *J* = 14.4, 9.6, 4.8 Hz, 1H), 2.07 – 1.88 (m, 1H), 1.81 – 1.70 (m, 2H), 1.32 – 1.26 (m, 1H), 1.16 (d, *J* = 10.0 Hz, 9H), 0.83 (d, *J* = 24.8 Hz, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 176.80, 176.67, 141.37, 140.88, 136.09, 128.64, 128.62, 128.30, 128.28, 127.95, 127.76, 127.28, 126.93, 83.95, 83.87, 80.30, 80.24, 66.42, 66.37, 46.90, 46.74, 40.79, 39.88, 39.88, 39.20, 31.05, 31.00, 29.53, 29.49, 26.63, 26.61. IR (cm<sup>-1</sup>): 3030, 2956, 2850, 1684, 1597, 1197, 756, 690.

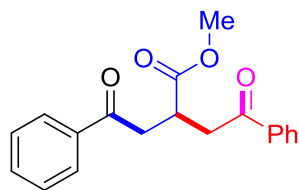
**(9b) methyl 5-methyl-4-oxo-2-(2-oxo-2-phenylethyl)hexanoate**



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.96 – 7.94 (m, 2H), 7.60 – 7.56 (m, 1H), 7.47 (dd, *J* = 10.4, 4.8 Hz, 2H), 3.69 (s, 3H), 3.49 – 3.43 (m, 2H), 3.28 (dd, *J* = 19.2, 8.0 Hz, 1H), 3.03 (dd, *J* = 18.0, 6.0 Hz, 1H), 2.82 (dd, *J* = 18.1, 5.9 Hz, 1H), 2.65 – 2.58 (m, 1H), 1.10 (dd, *J* = 6.8, 2.8 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 212.67, 197.92, 174.94, 136.56, 133.48, 128.77, 128.18, 52.24, 41.03 (d, *J* = 9.5 Hz), 39.55, 35.71, 18.25. IR (cm<sup>-1</sup>): 3061, 1969, 1874, 1732, 1684, 1597, 757, 691. HRMS: calcd. for C<sub>16</sub>H<sub>20</sub>O<sub>4</sub>Na<sup>+</sup> [M+Na]<sup>+</sup>: 299.1254; Found: 299.1262.

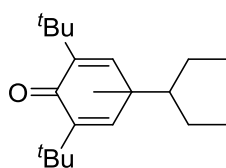
**(9i) methyl 4-oxo-2-(2-oxo-2-phenylethyl)-4-phenylbutanoate**<sup>8</sup>





M.p. 72-73.5 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 – 7.93 (m, 4H), 7.63 – 7.52 (m, 2H), 7.50 – 7.41 (m, 4H), 3.71 (s, 3H), 3.70 – 3.62 (m, 1H), 3.58 (dd,  $J = 18.0, 5.6$  Hz, 2H), 3.38 (dd,  $J = 18.0, 6.4$  Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  197.95, 174.99, 136.56, 133.49, 128.76, 128.21, 52.32, 39.61, 35.95. IR ( $\text{cm}^{-1}$ ): 3060, 2951, 1736, 1684, 1596, 1580, 1448, 1403, 1362, 1335, 1268, 1220, 1000, 754, 688.

**(10) 2,6-di-*tert*-butyl-4-methyl-4-(pentan-3-yl)cyclohexa-2,5-dien-1-one**<sup>9</sup>

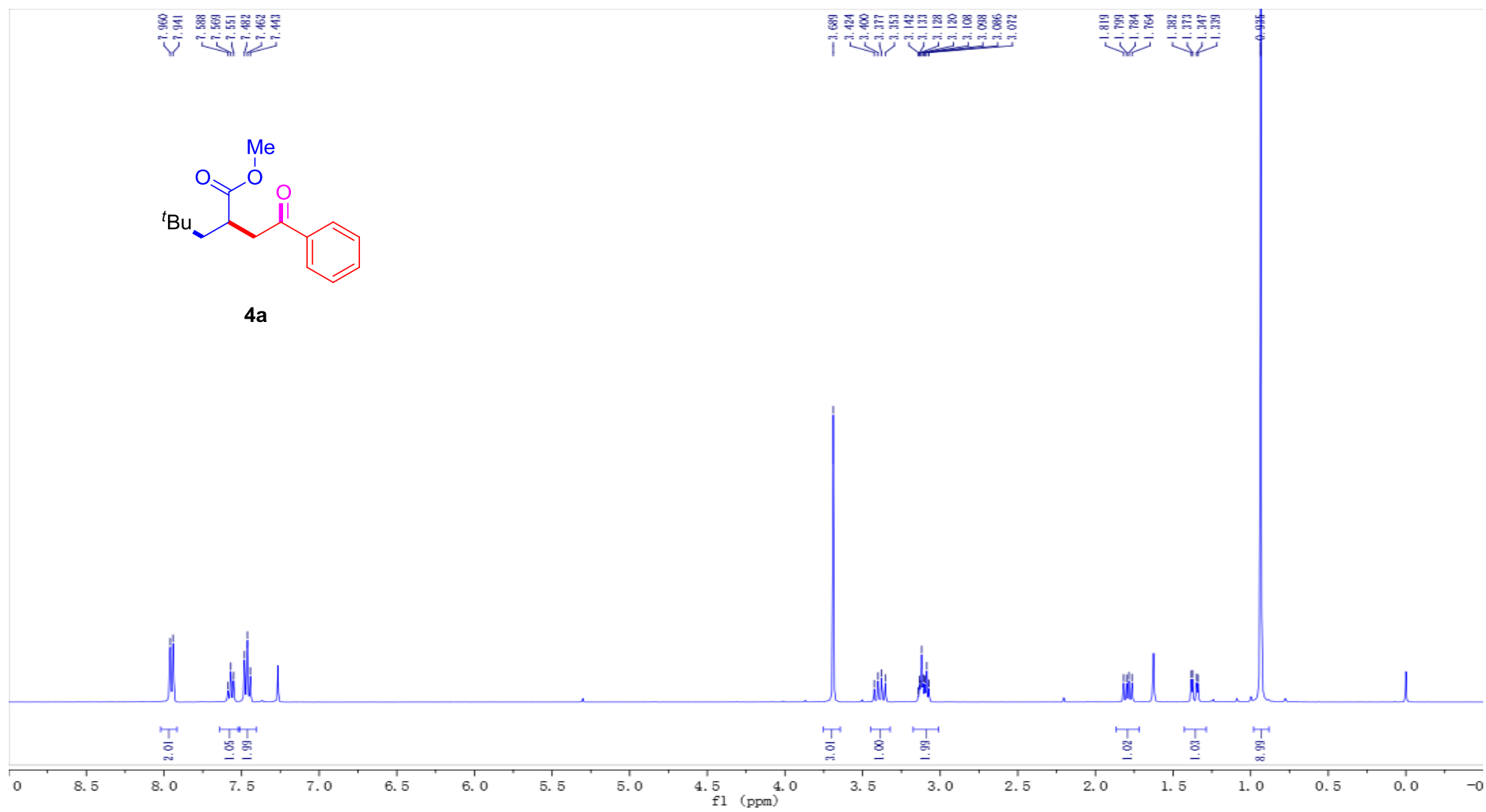


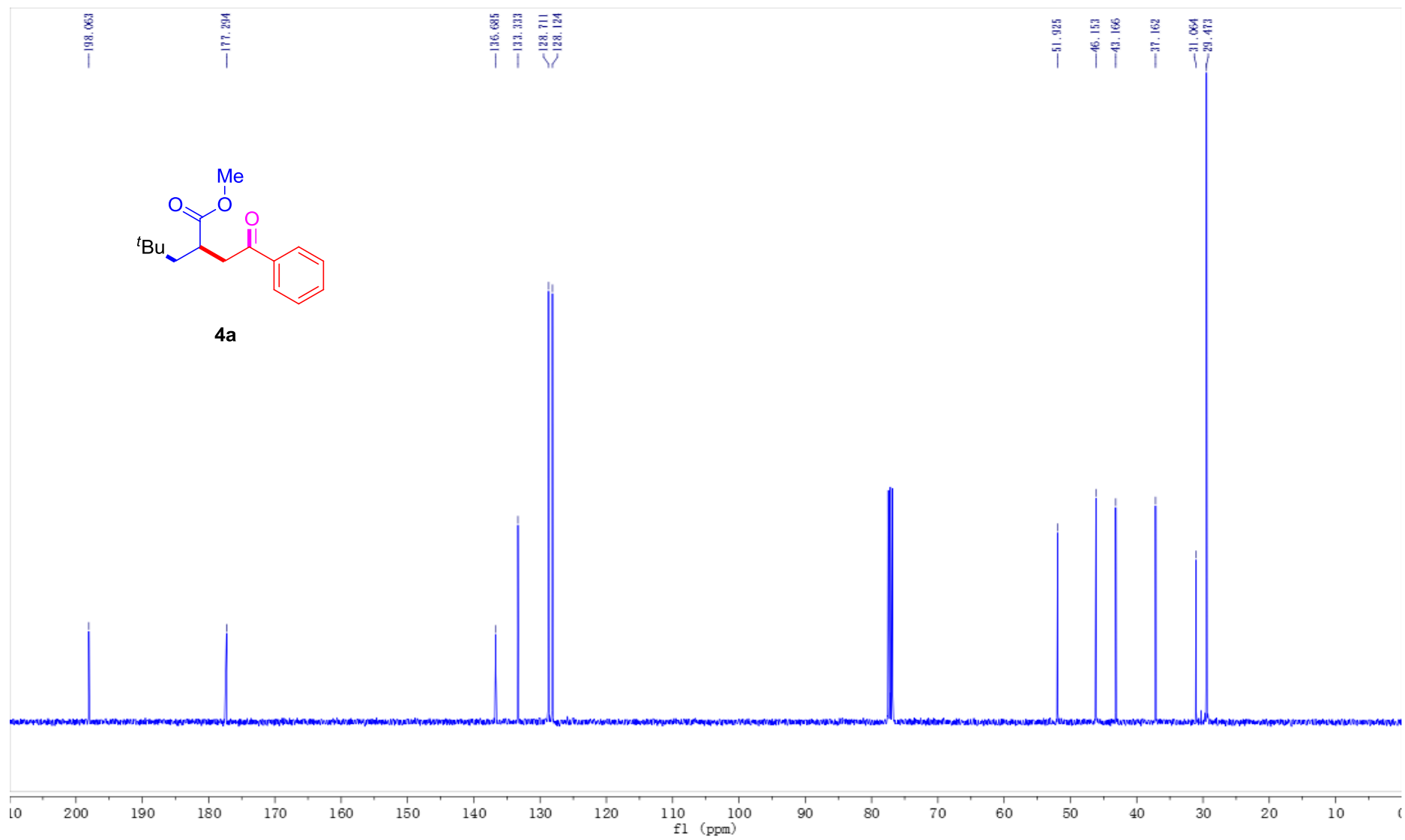
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.48 (s, 2H), 1.46 – 1.38 (m, 1H), 1.23 (s, 18H), 1.17 (s, 3H), 1.15 – 1.05 (m, 4H), 0.88 (t,  $J = 7.2$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  186.93, 146.67, 146.22, 51.58, 43.55, 34.82, 29.59, 25.16, 23.12, 13.94.

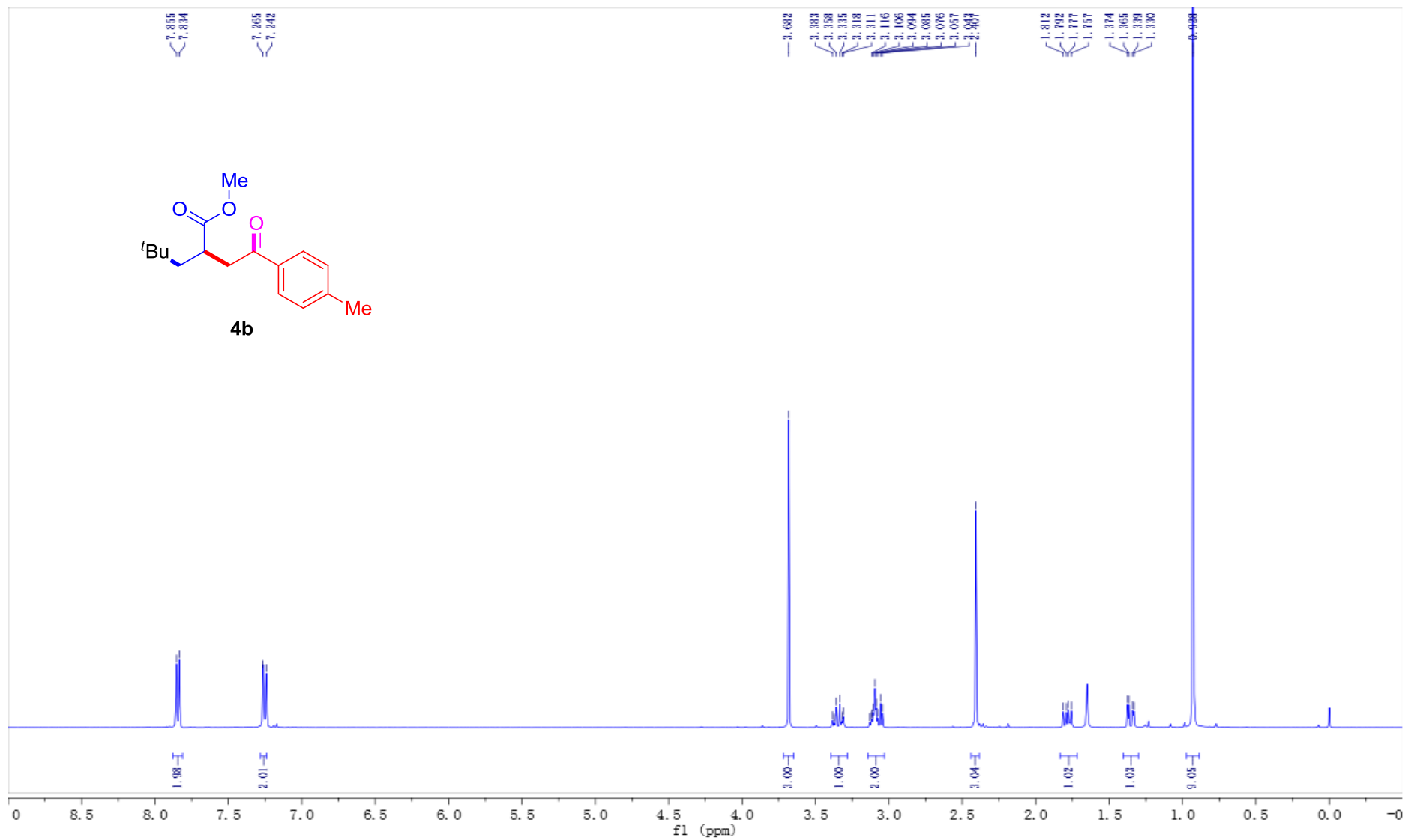
## V. References

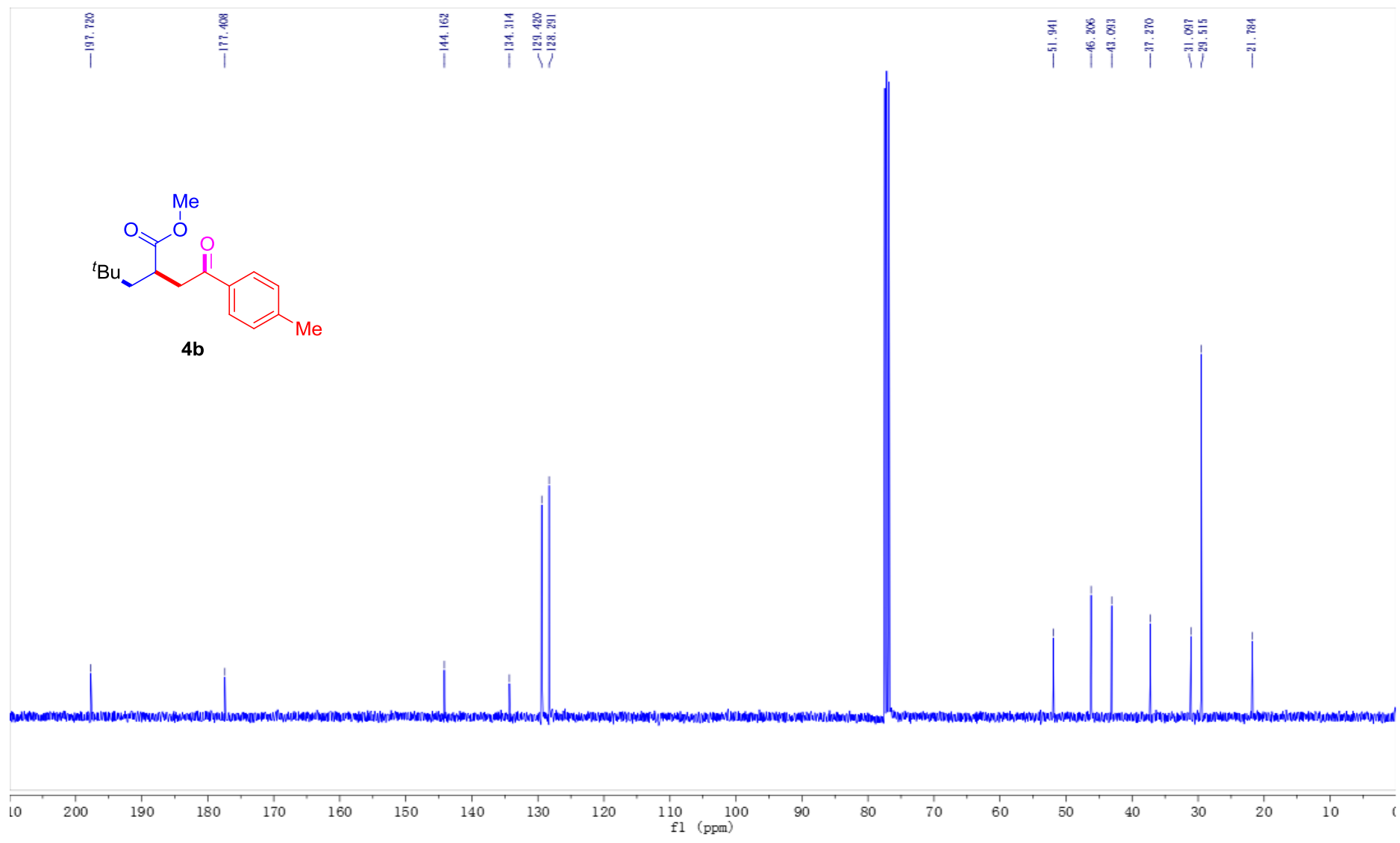
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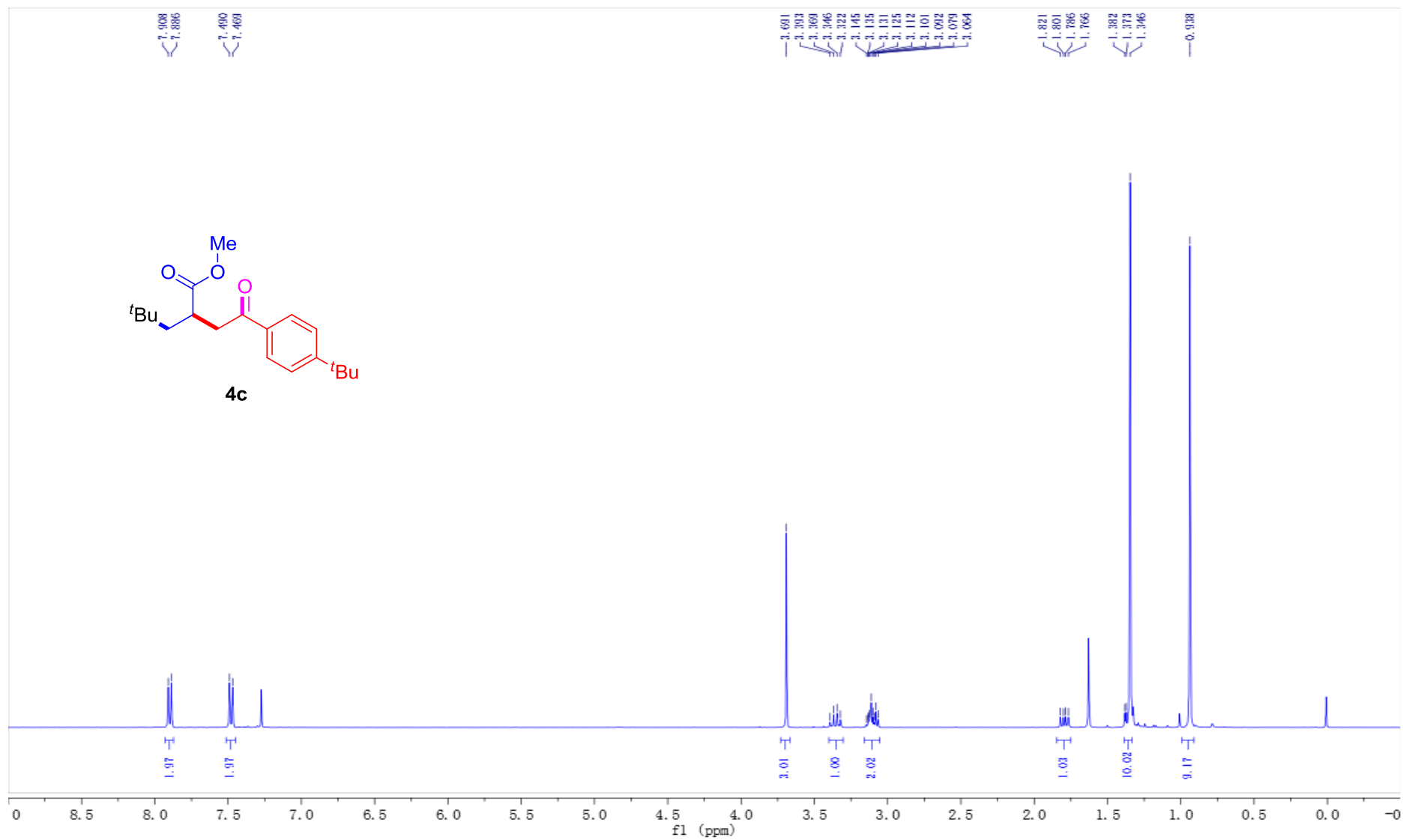
## VI. Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of products 4a-4l, 5b-5k, 6b-6g, 7, 8, 5c', 9b, 9i, 10.

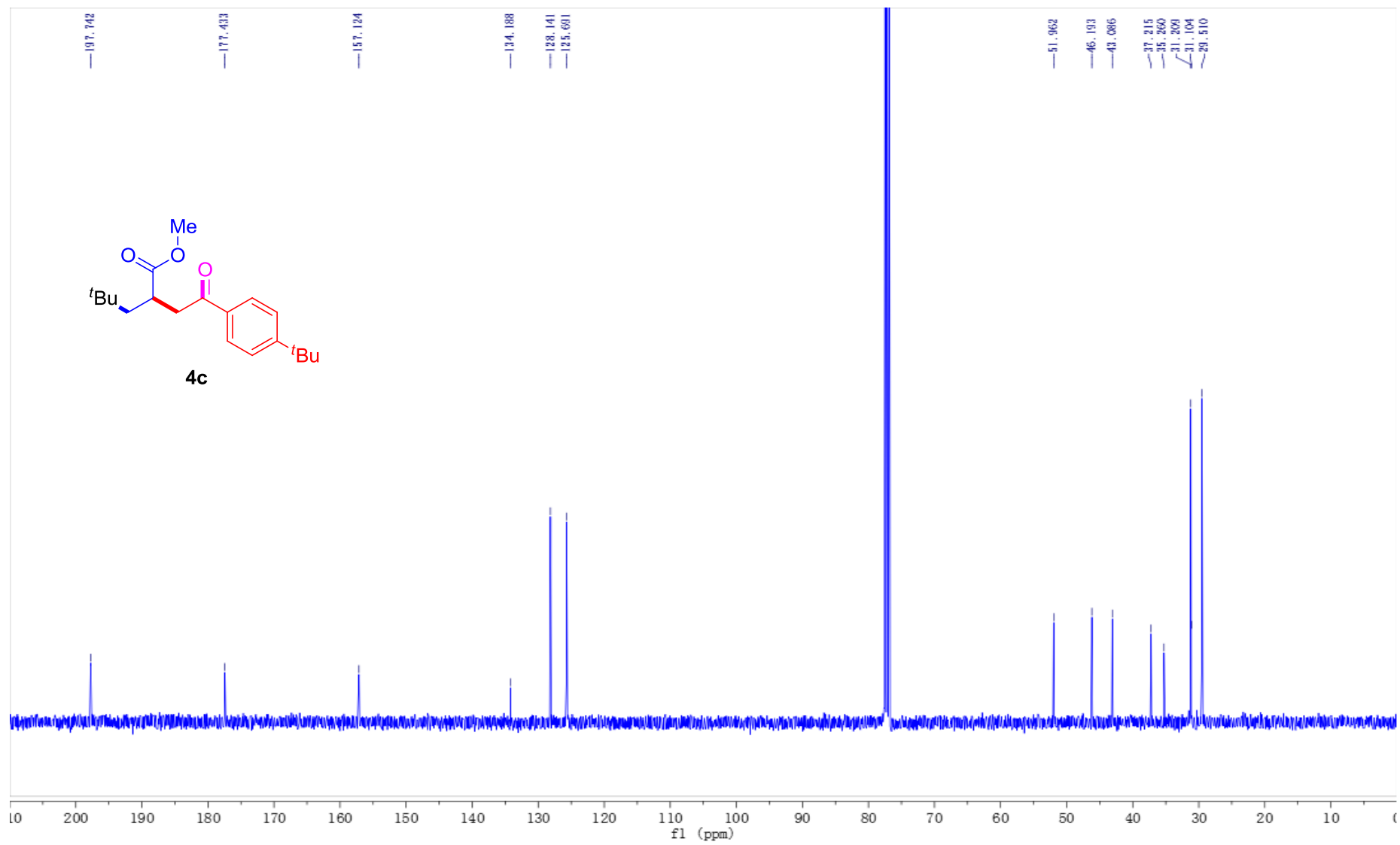


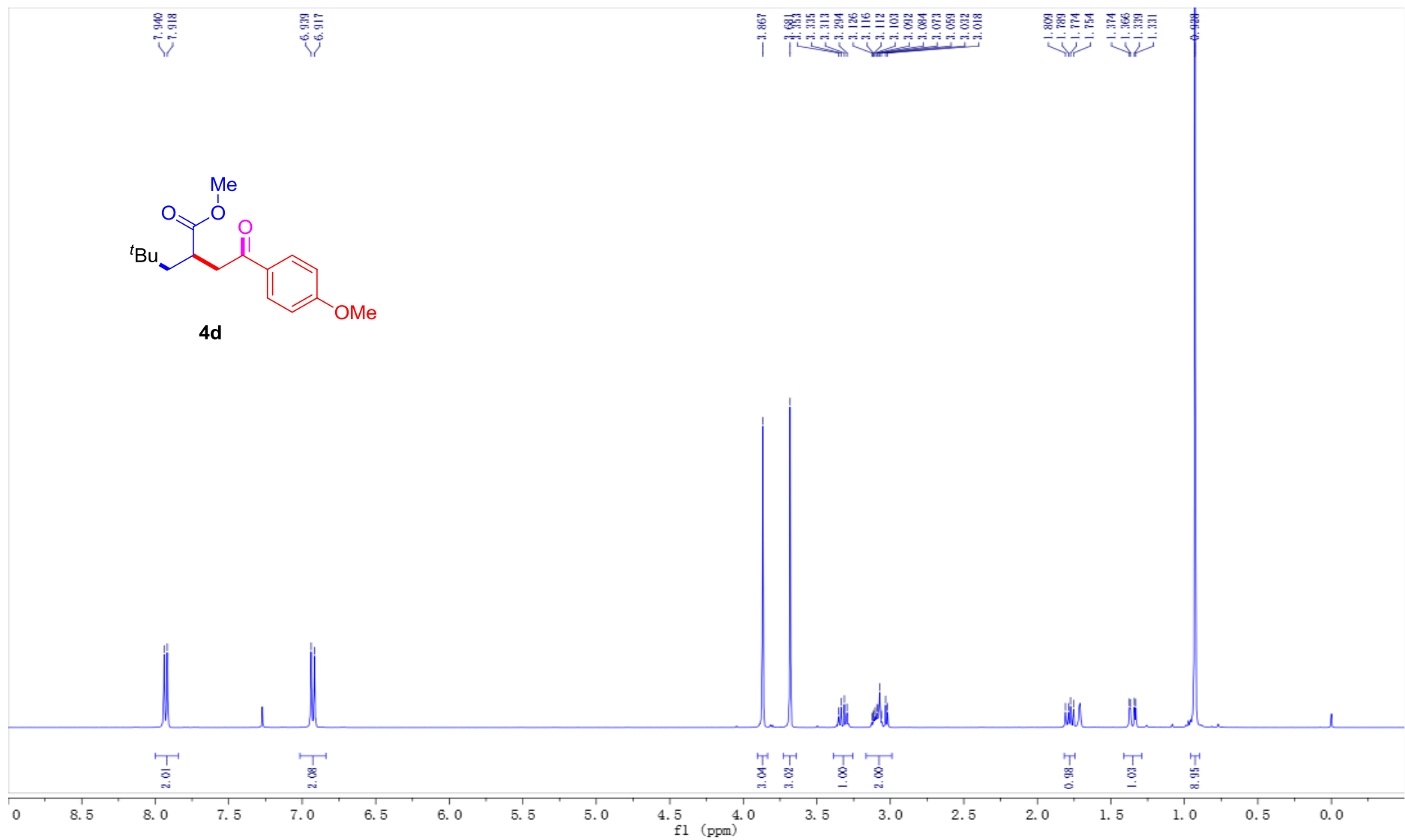




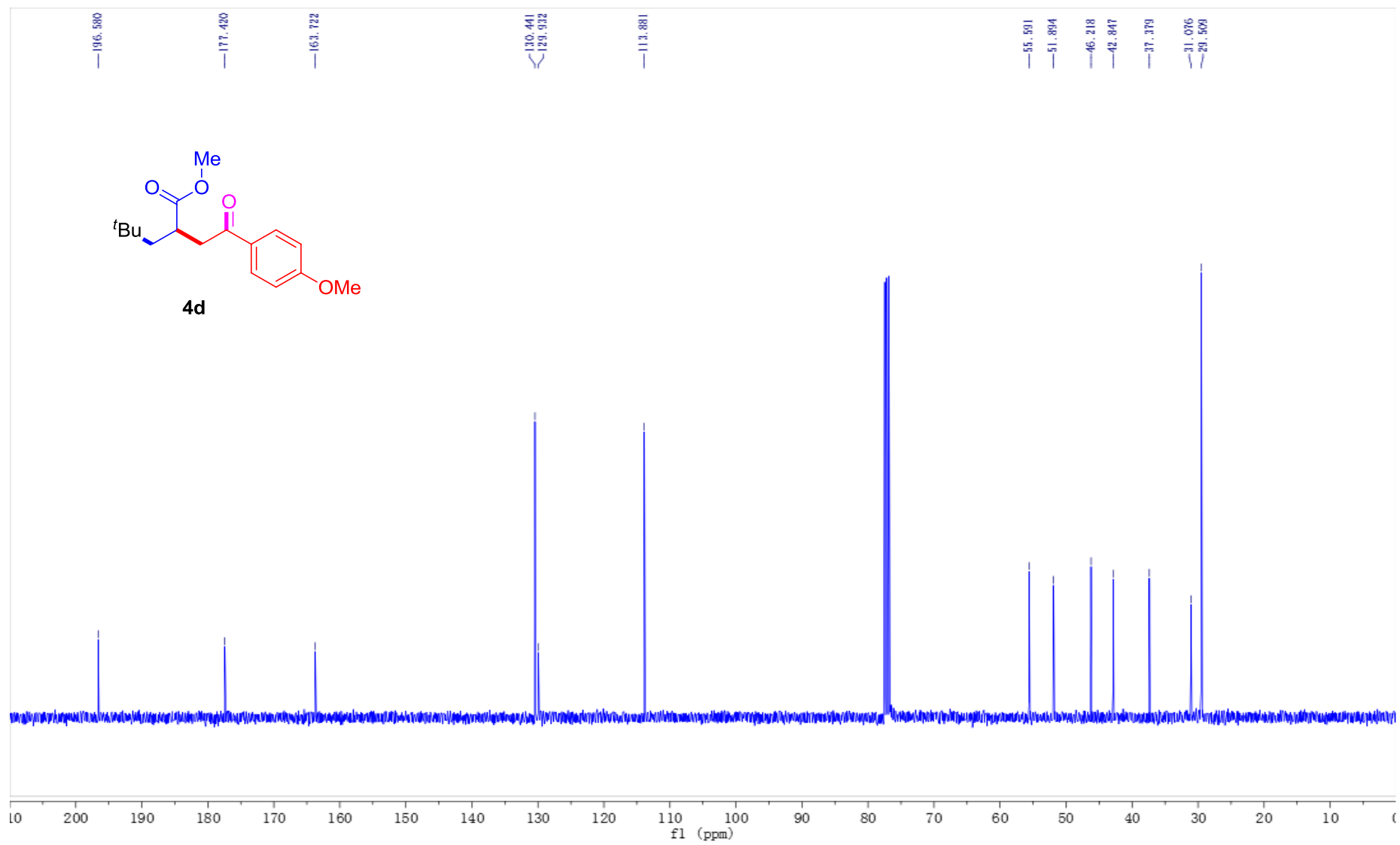


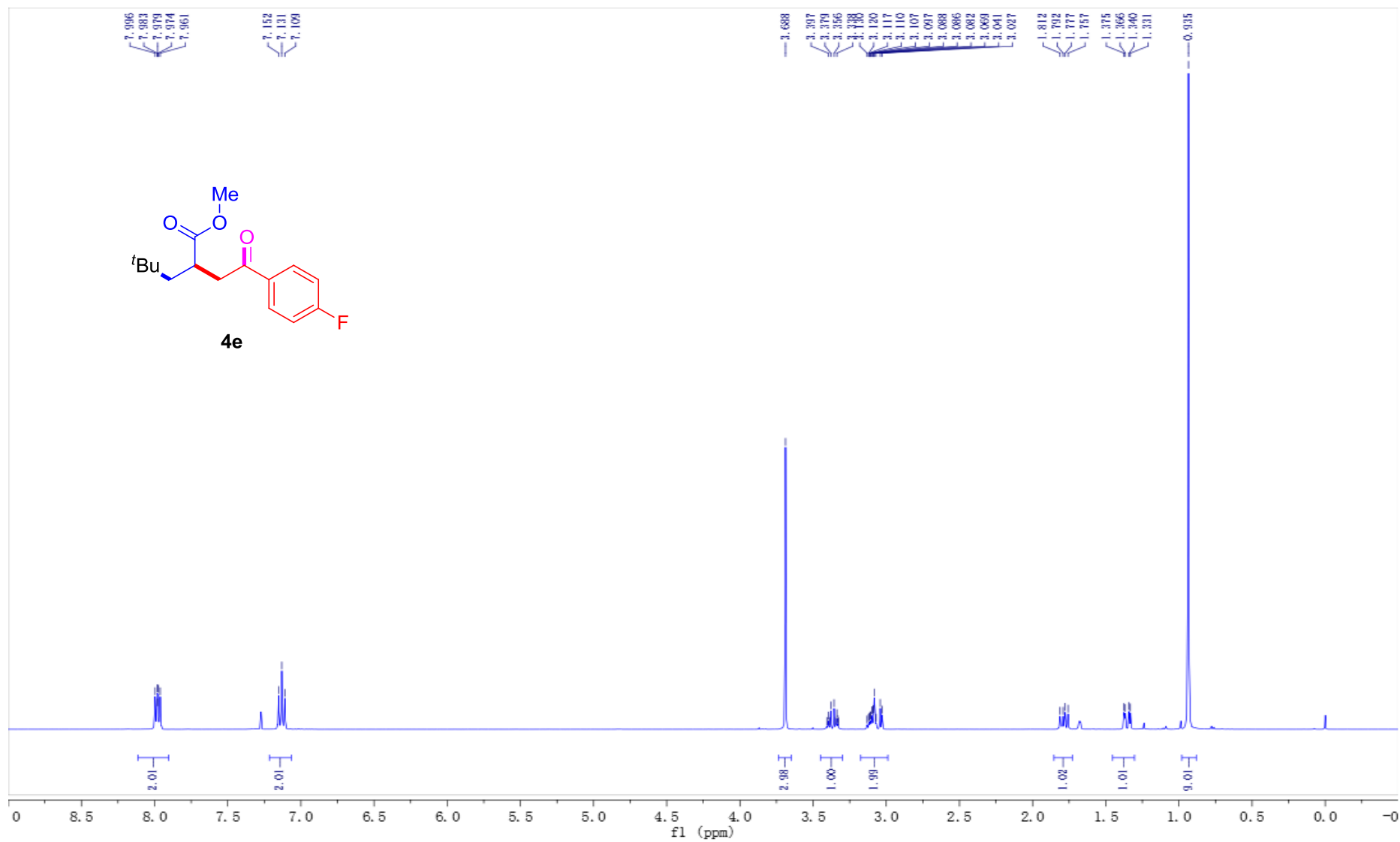


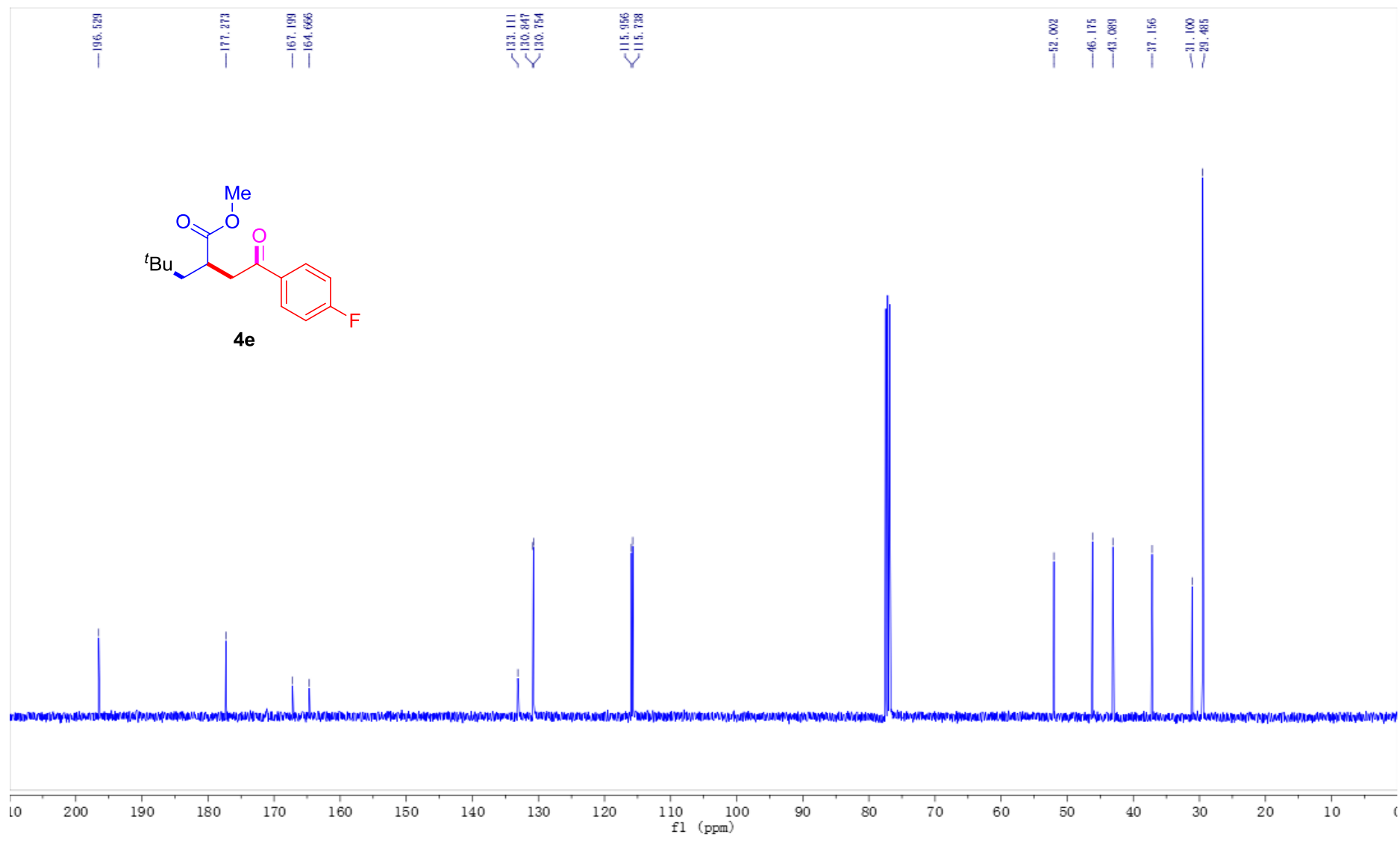


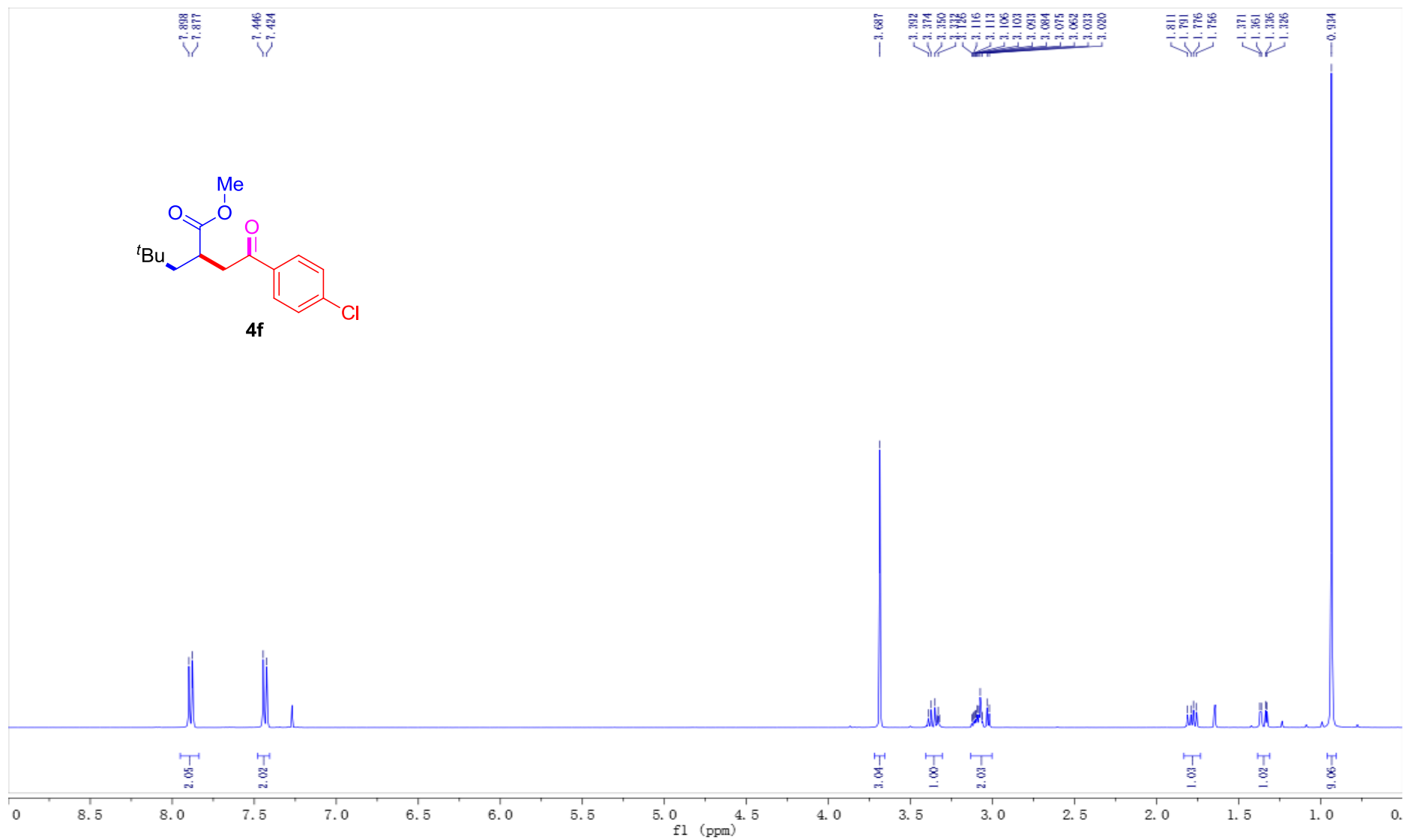


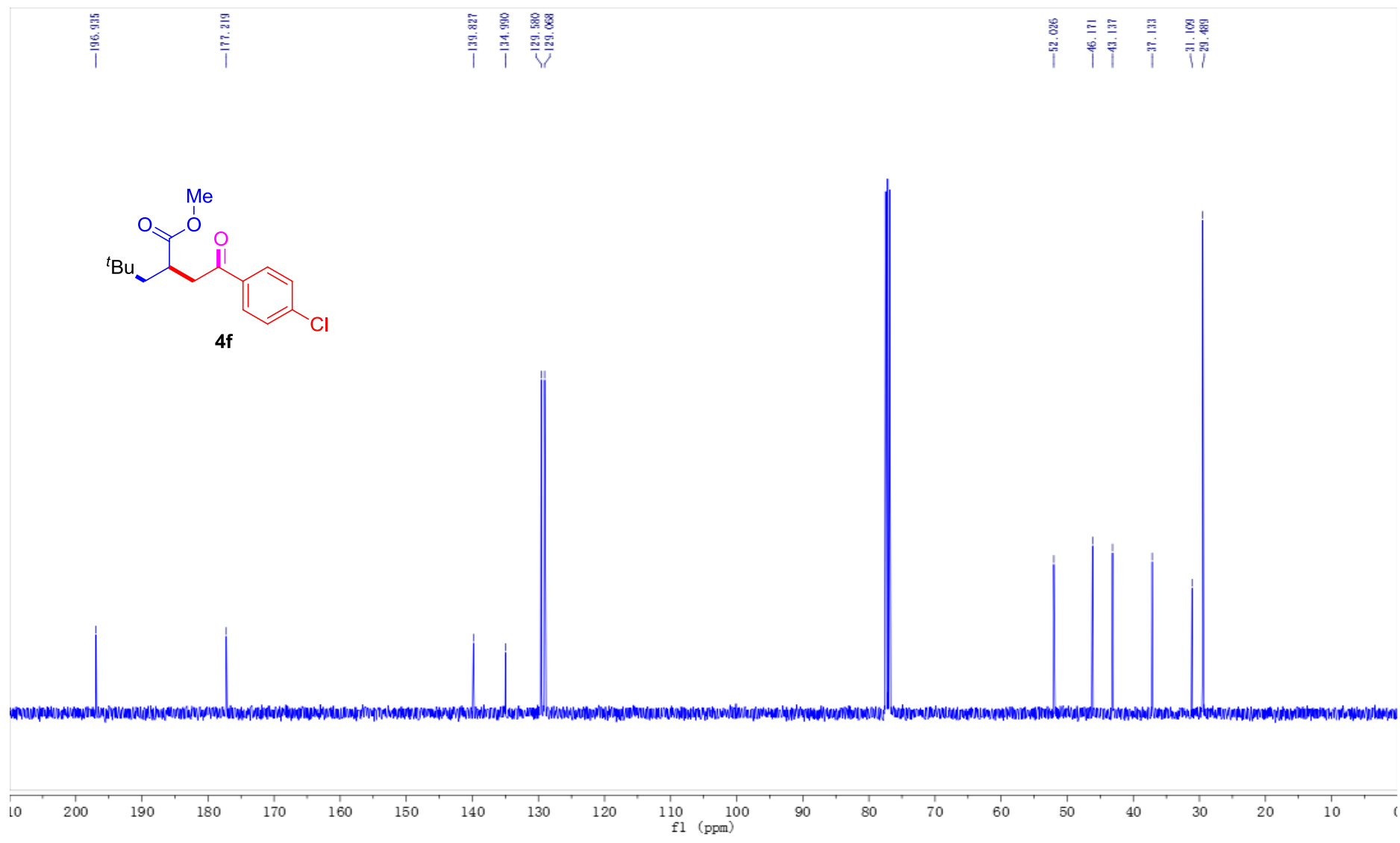


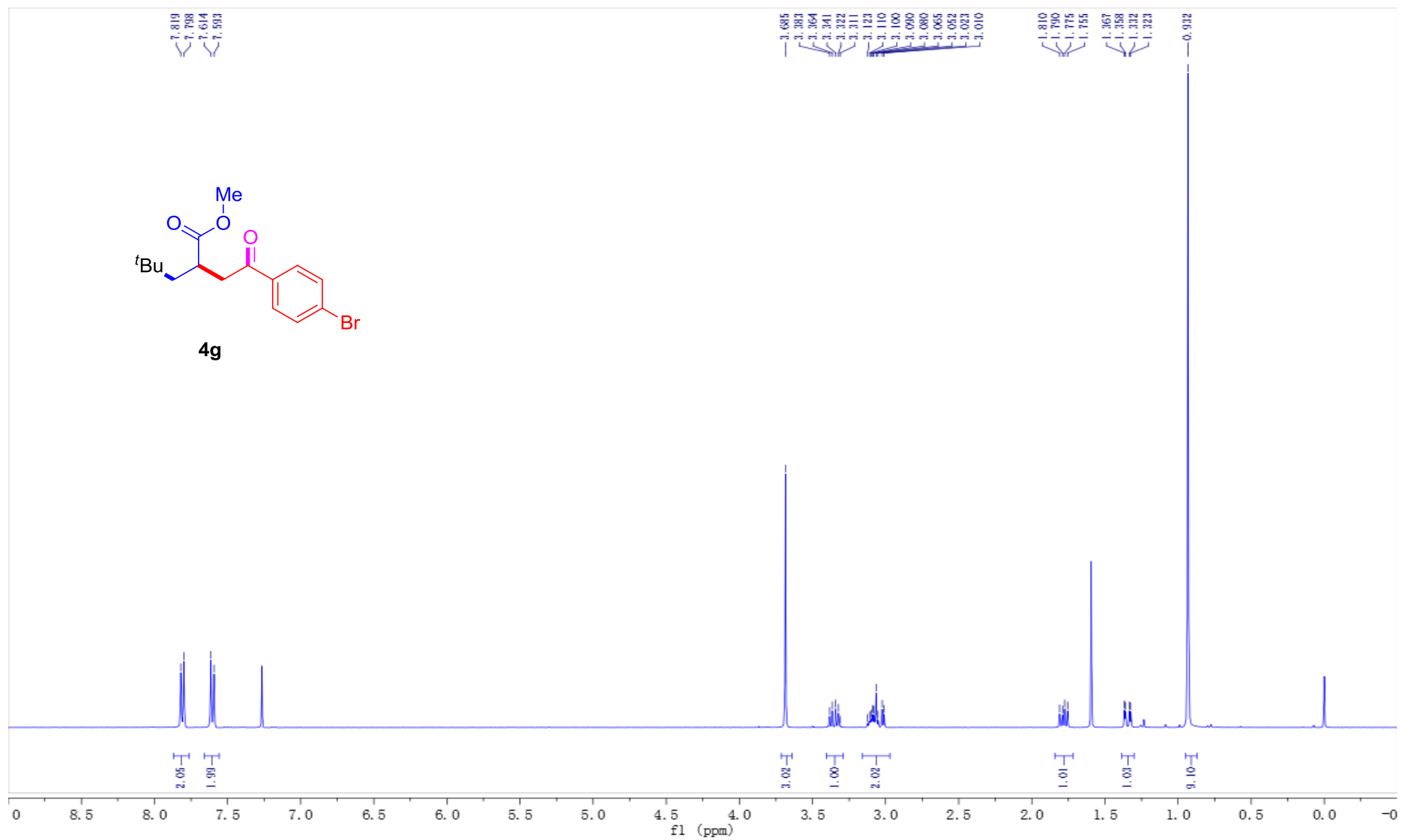


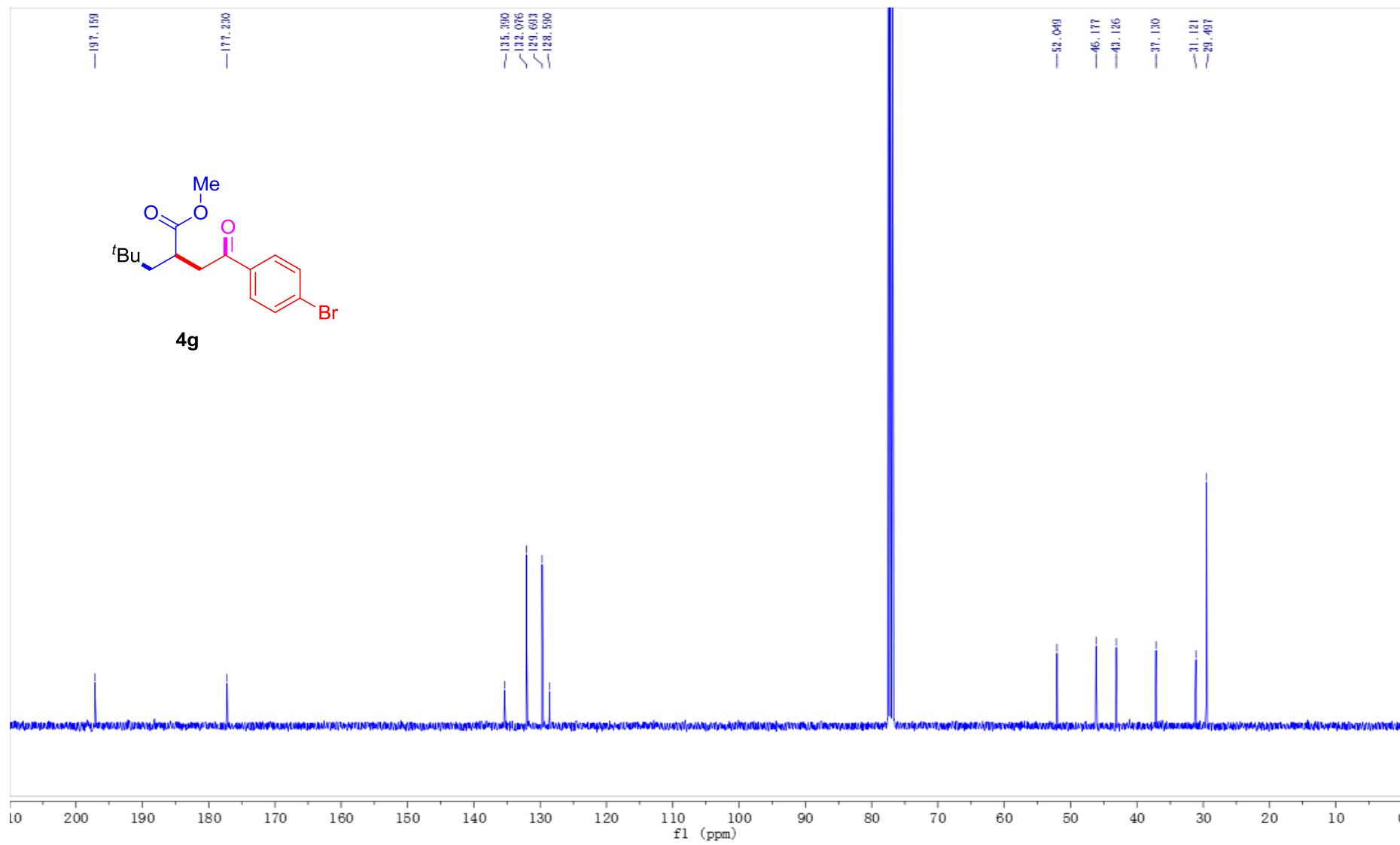


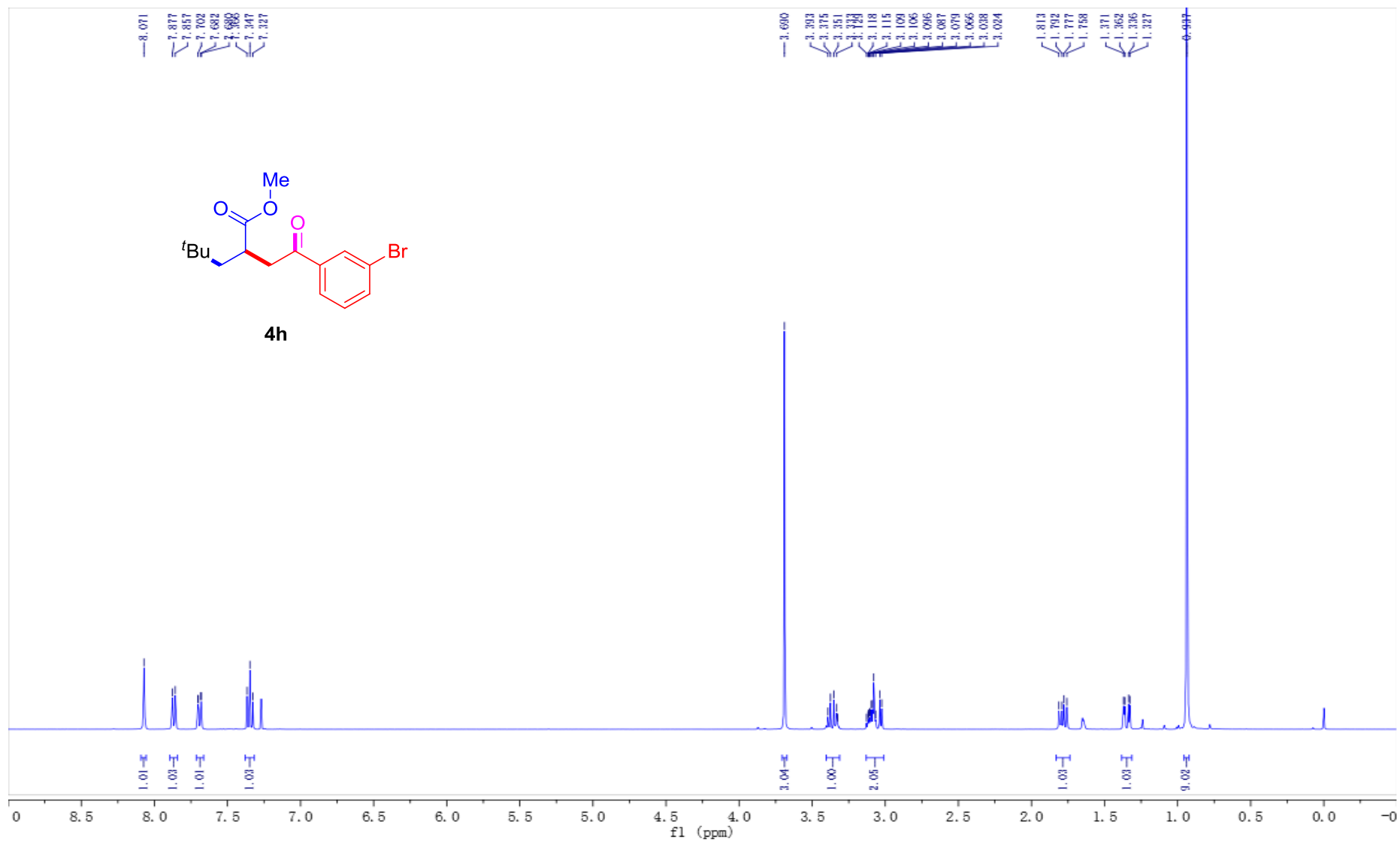




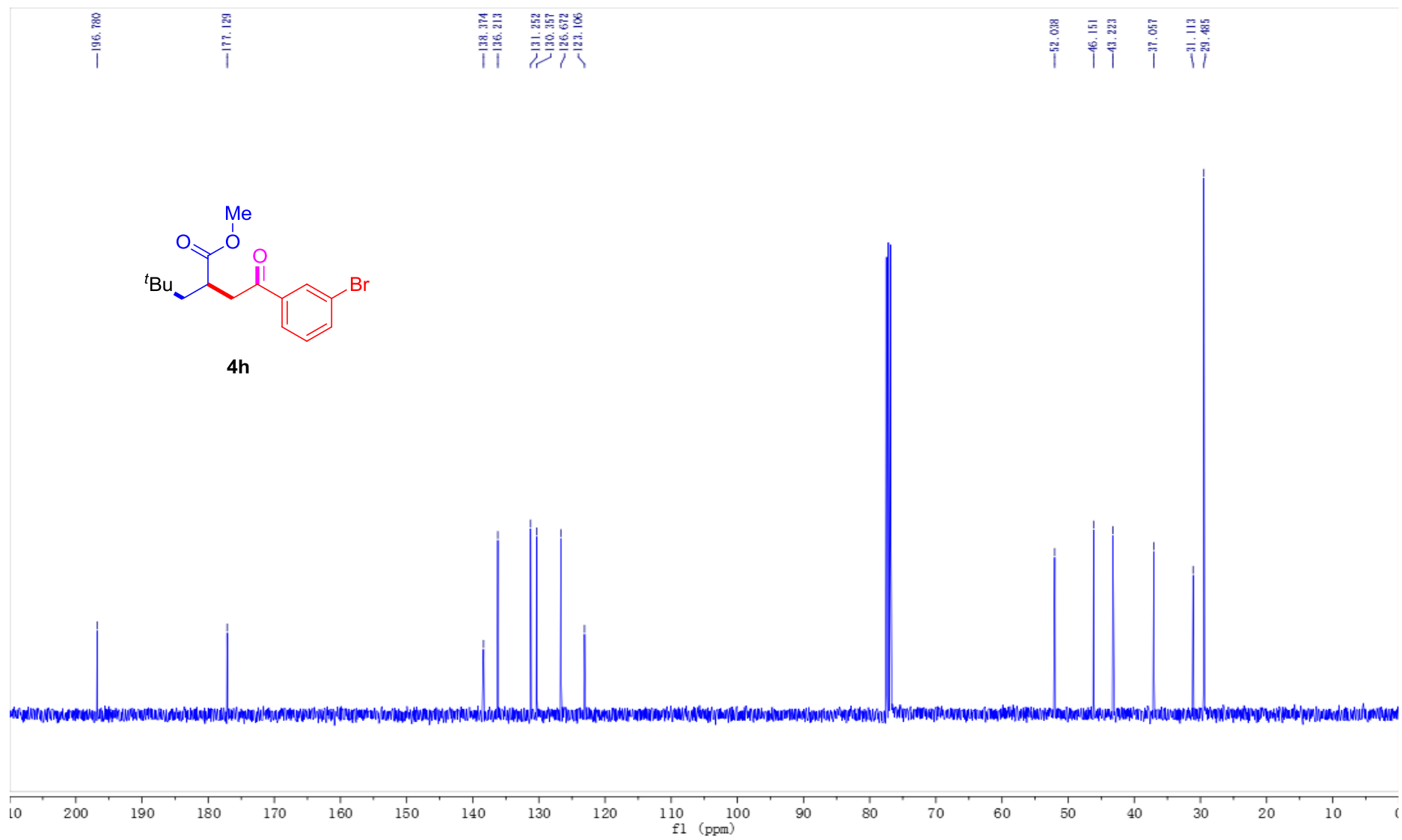


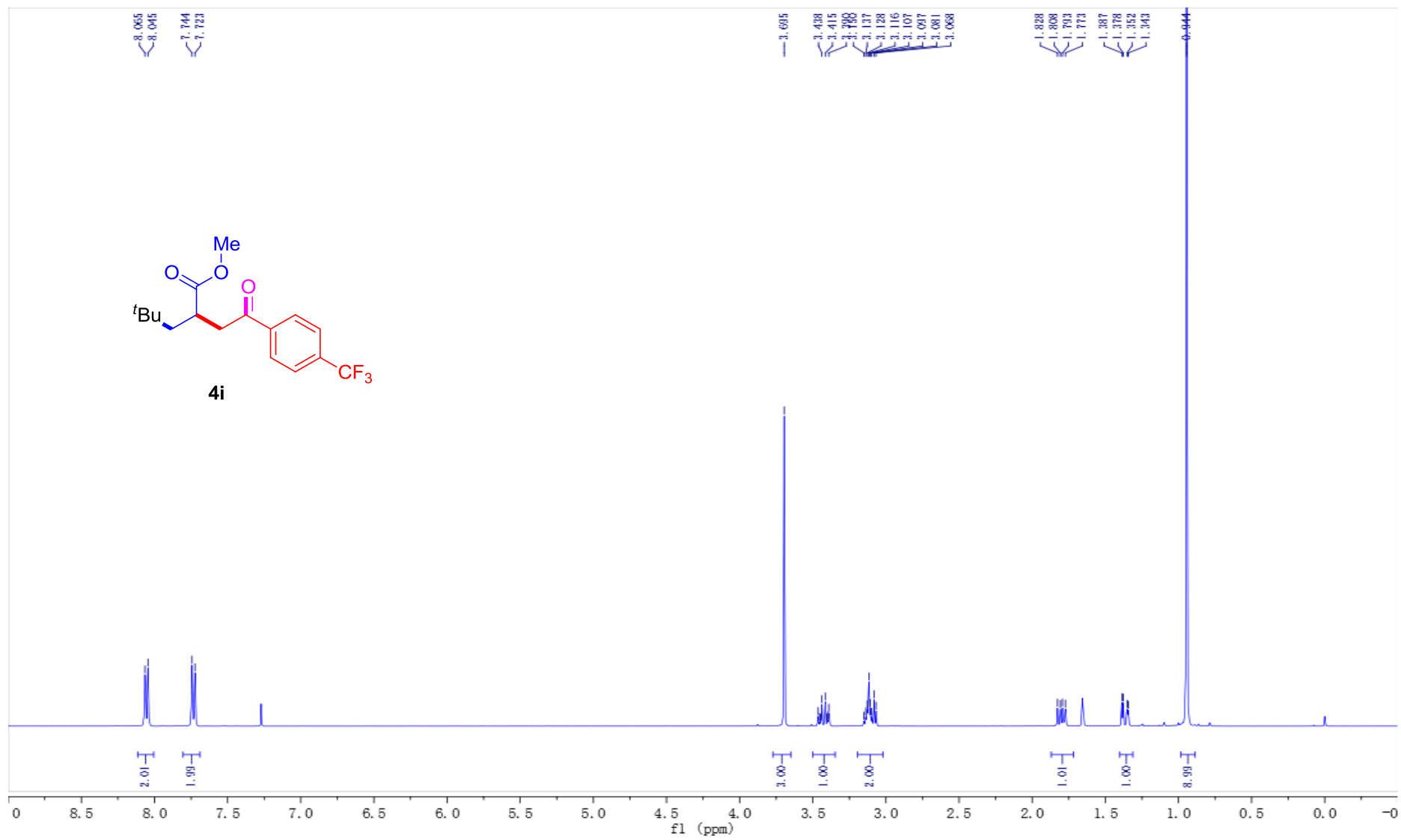


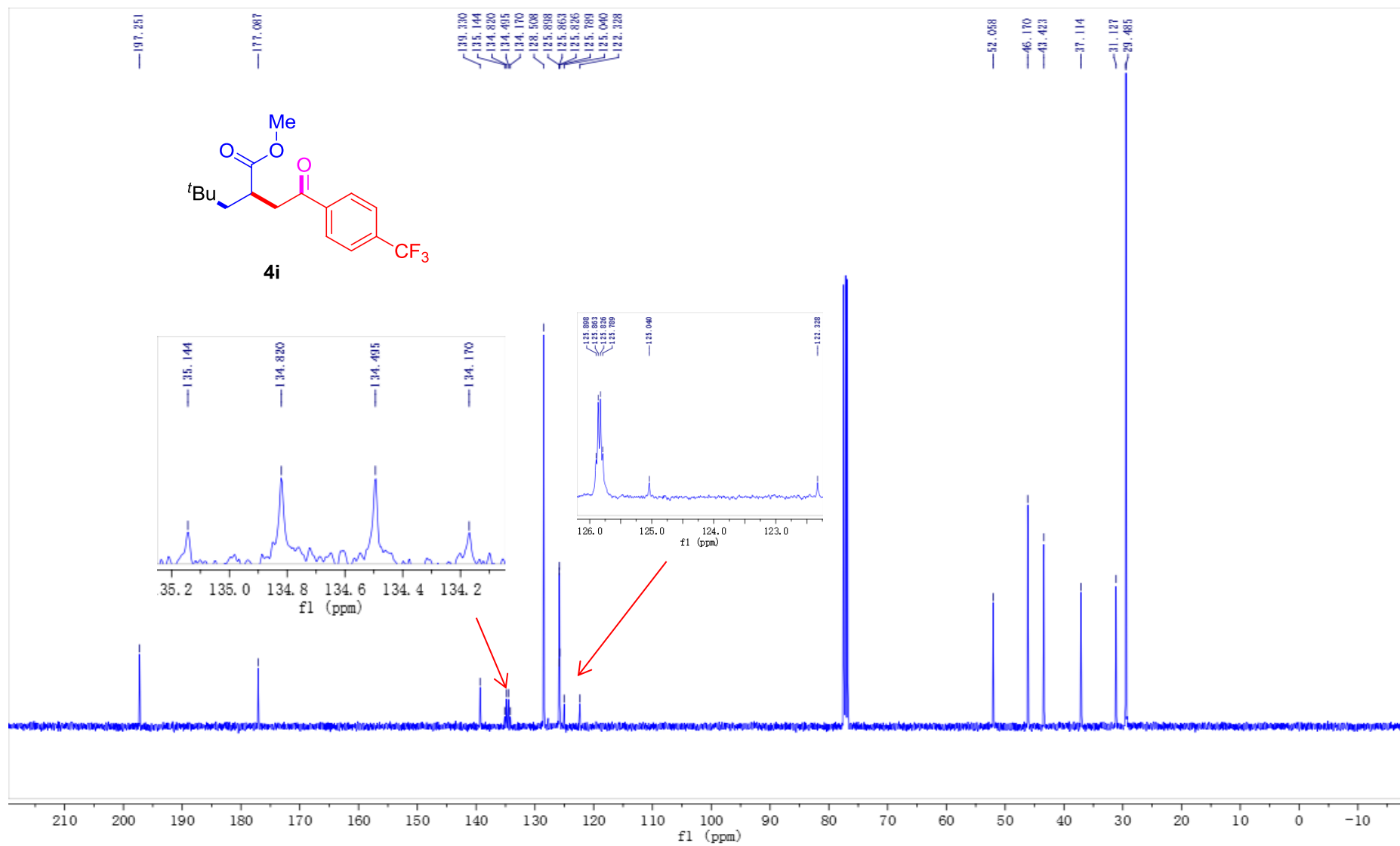


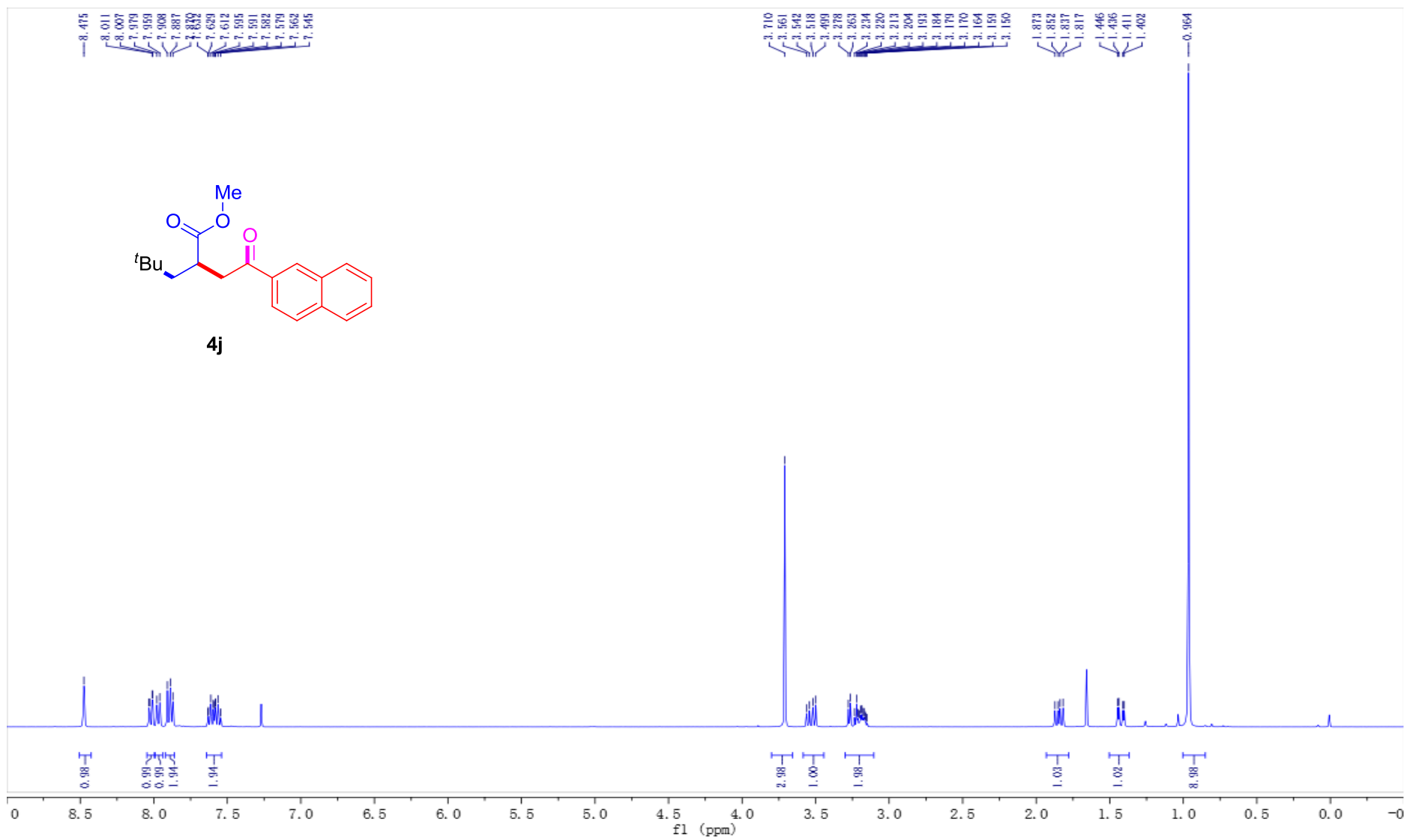


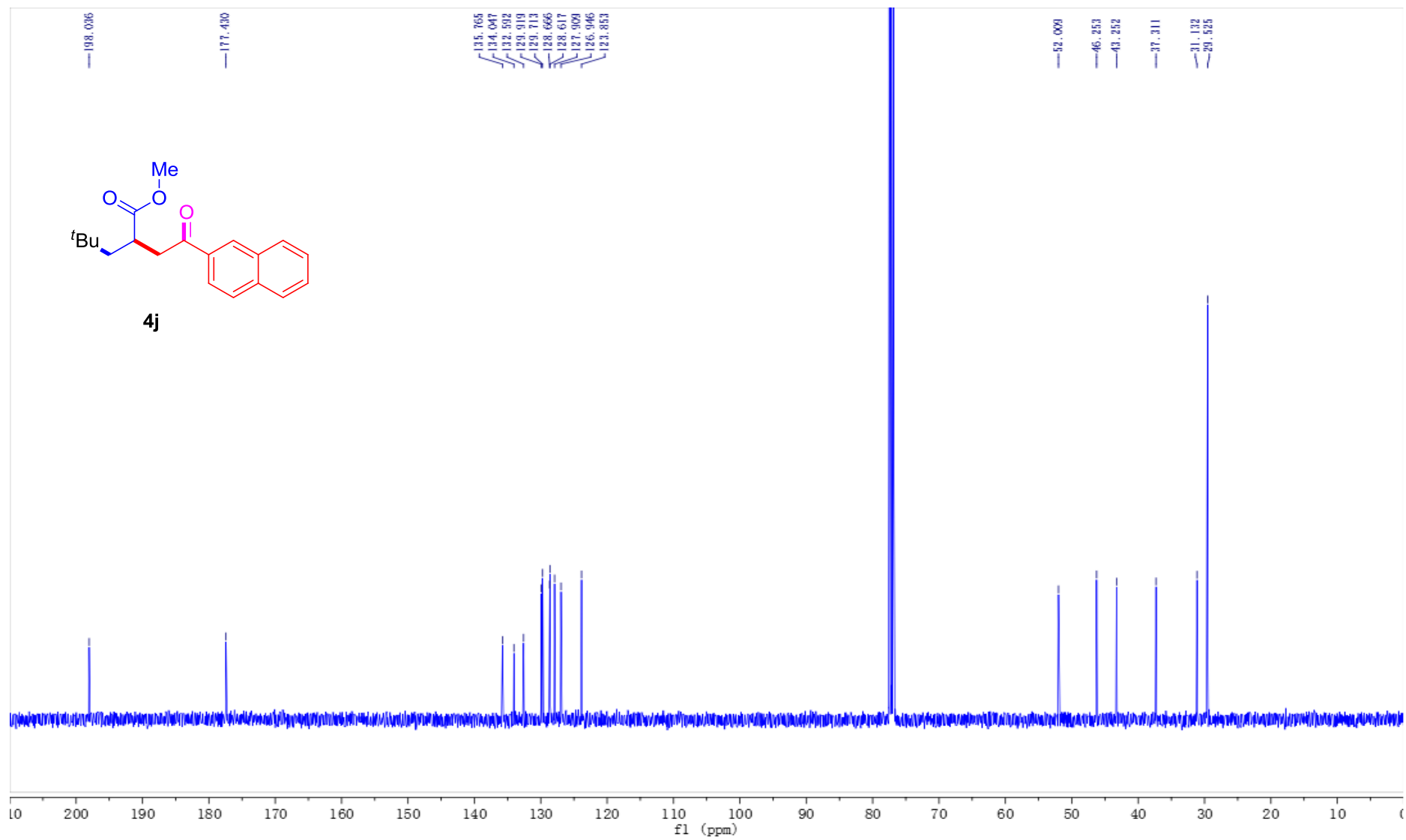


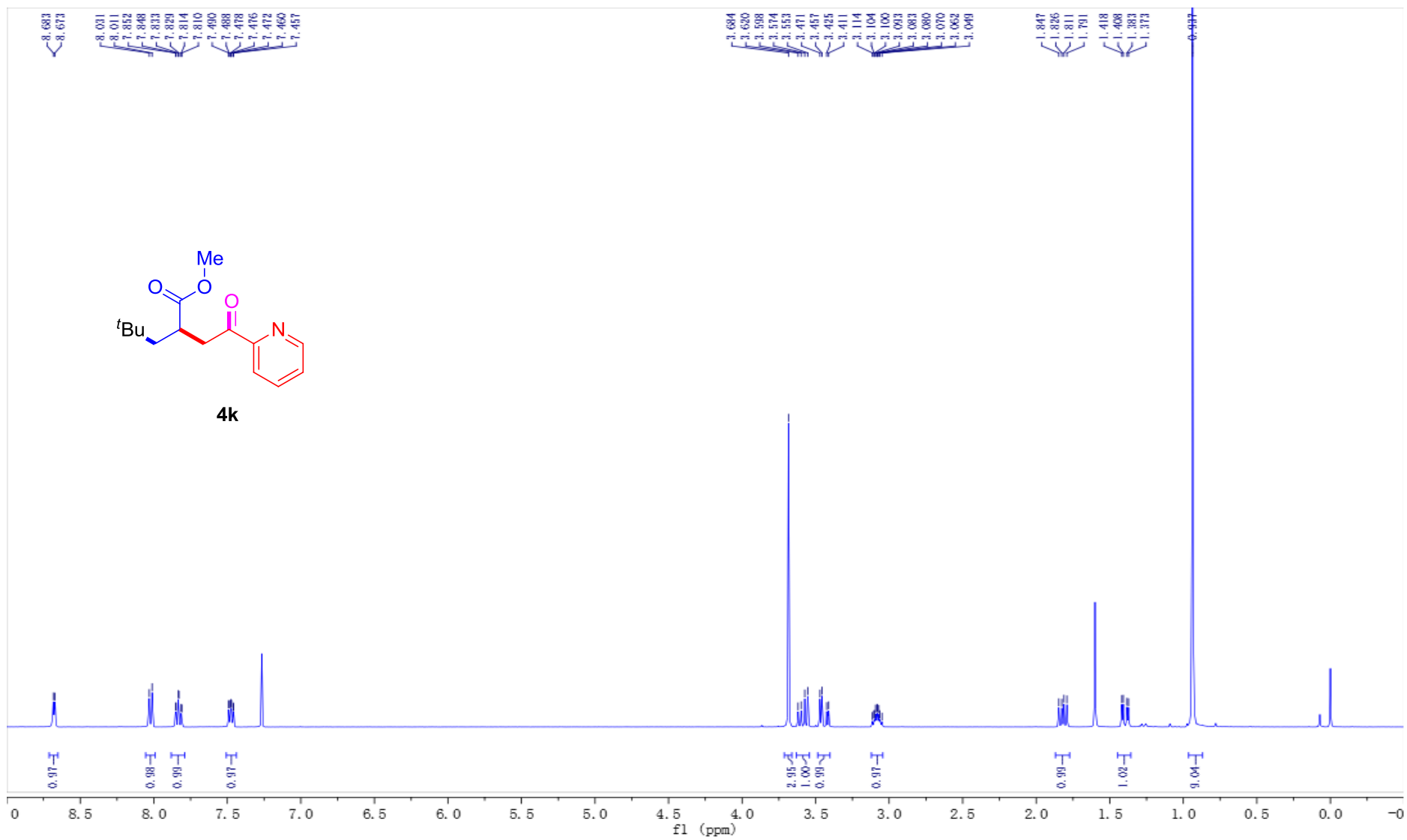


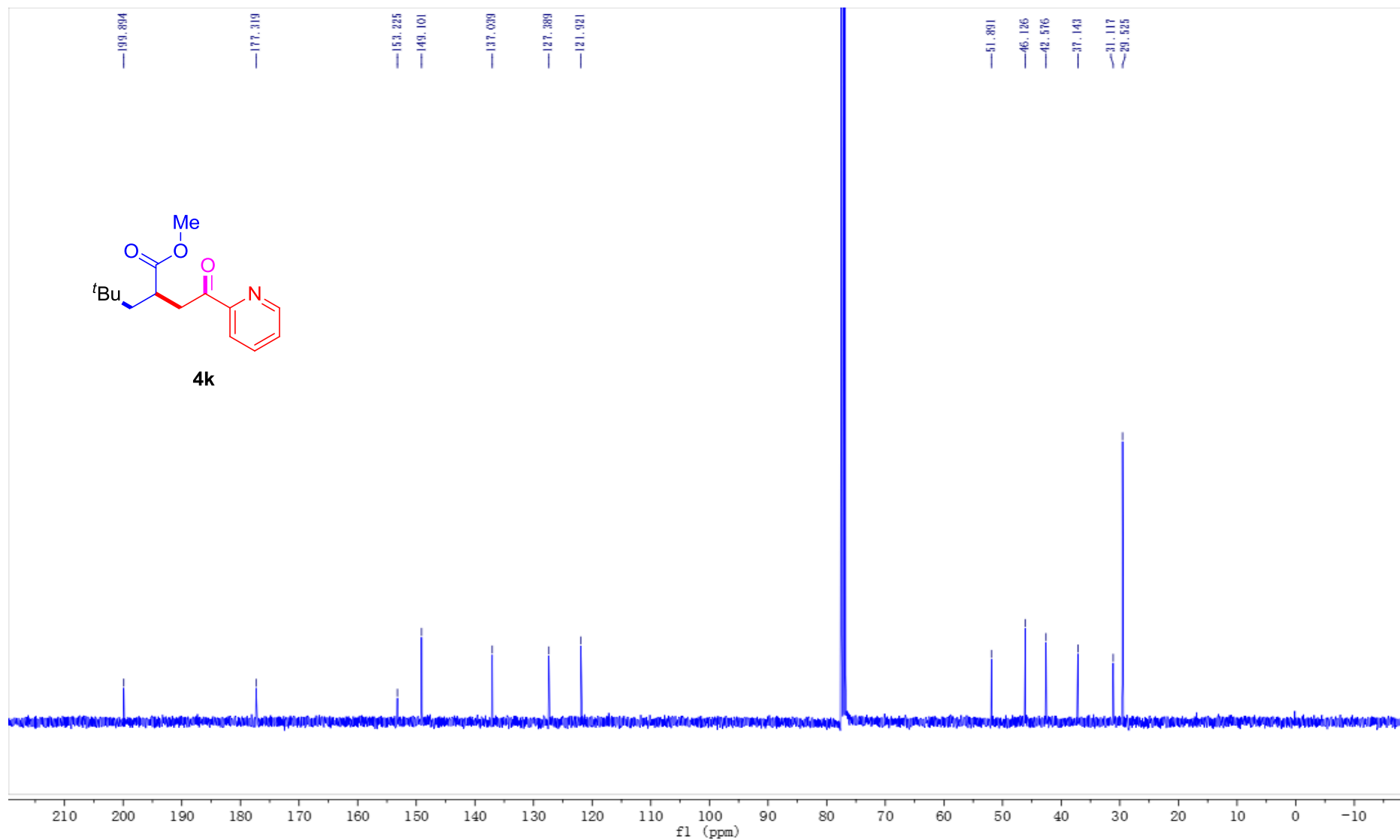


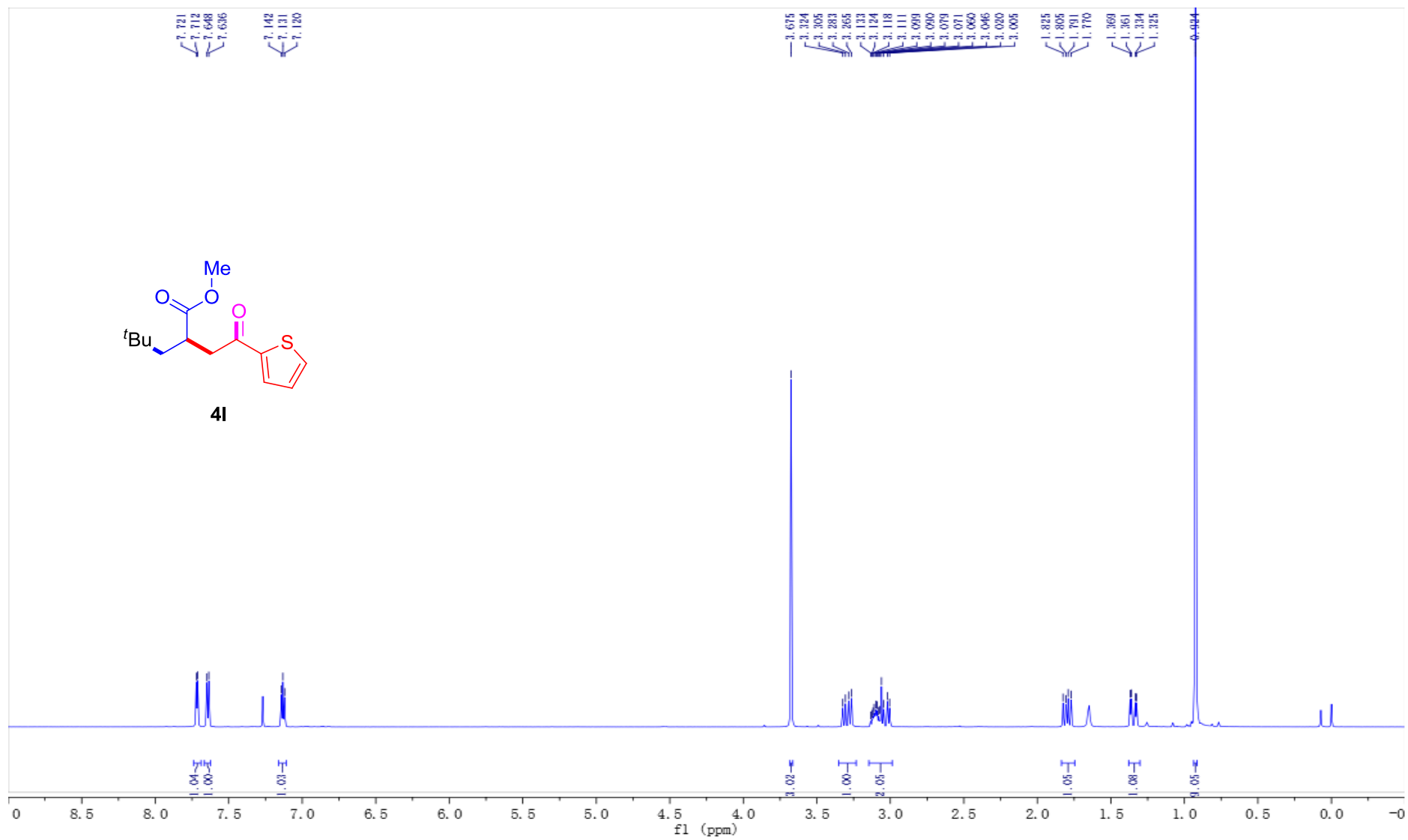




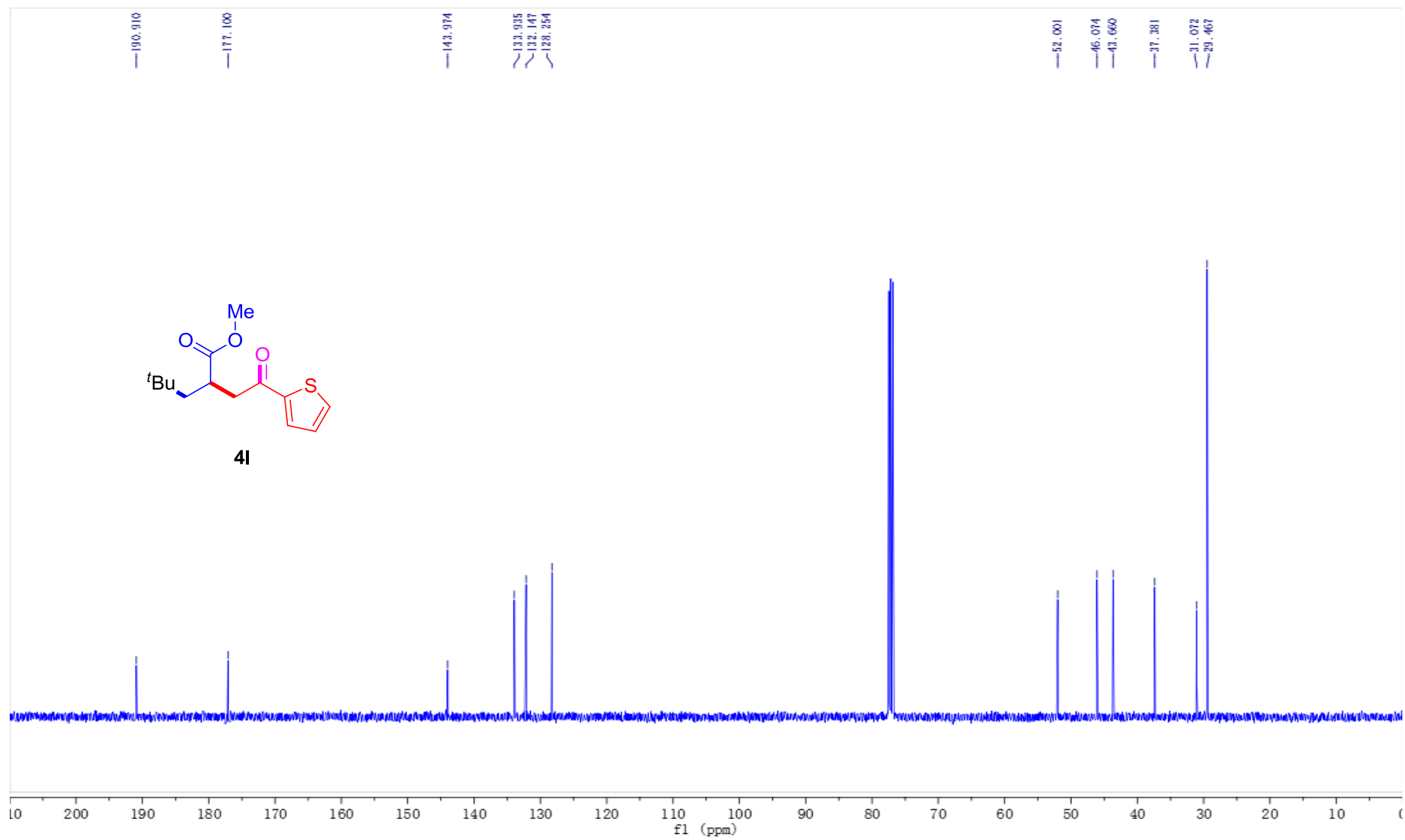


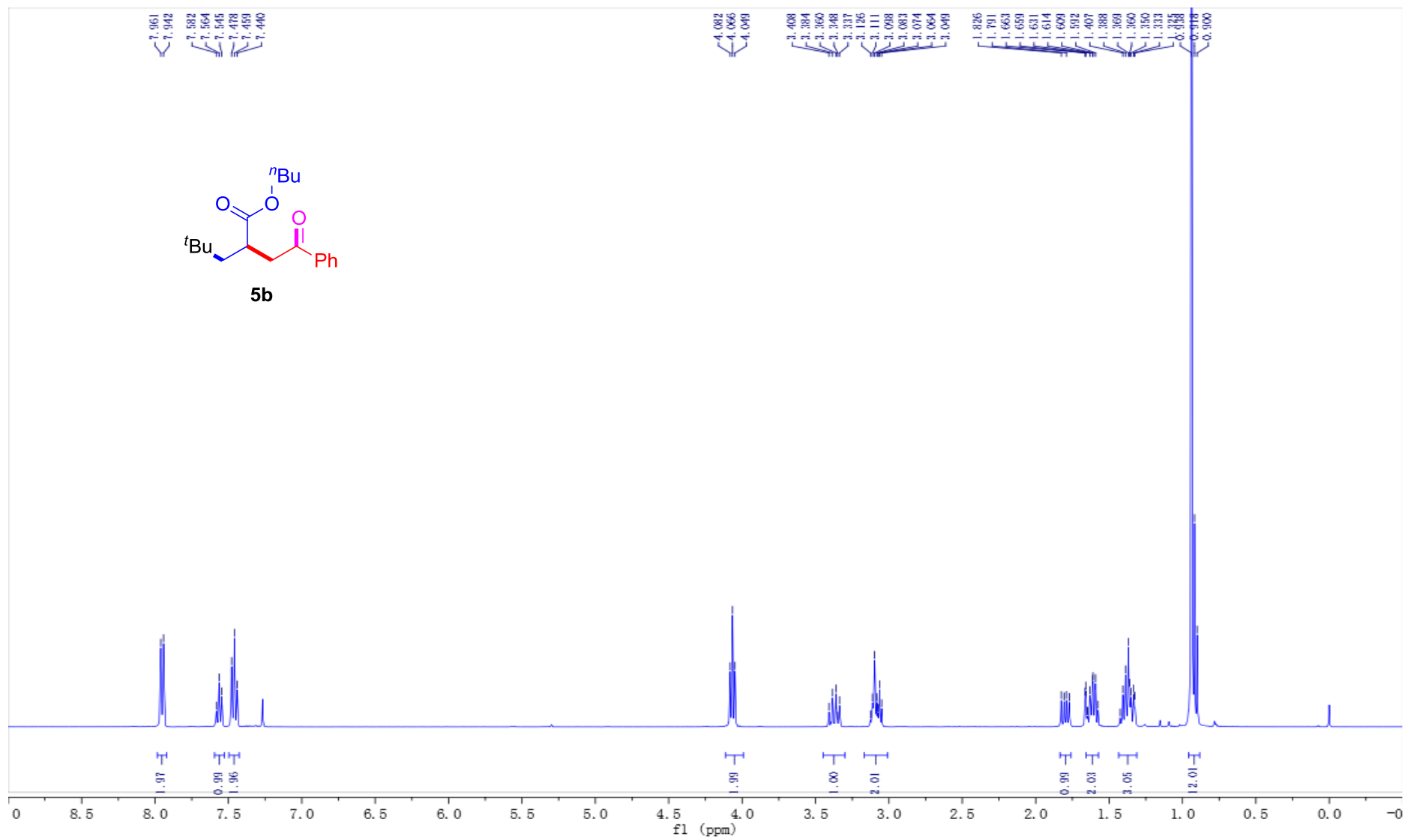


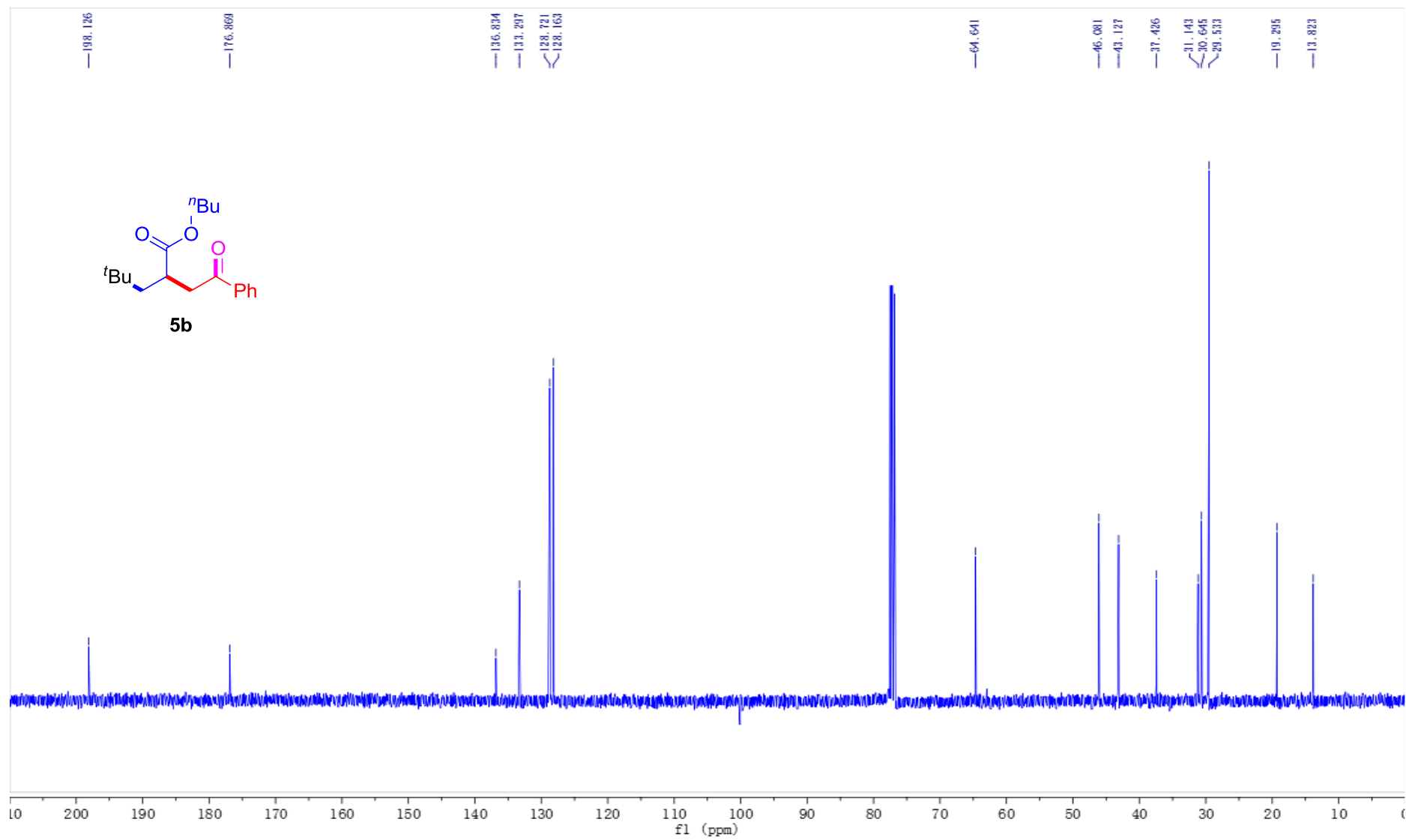


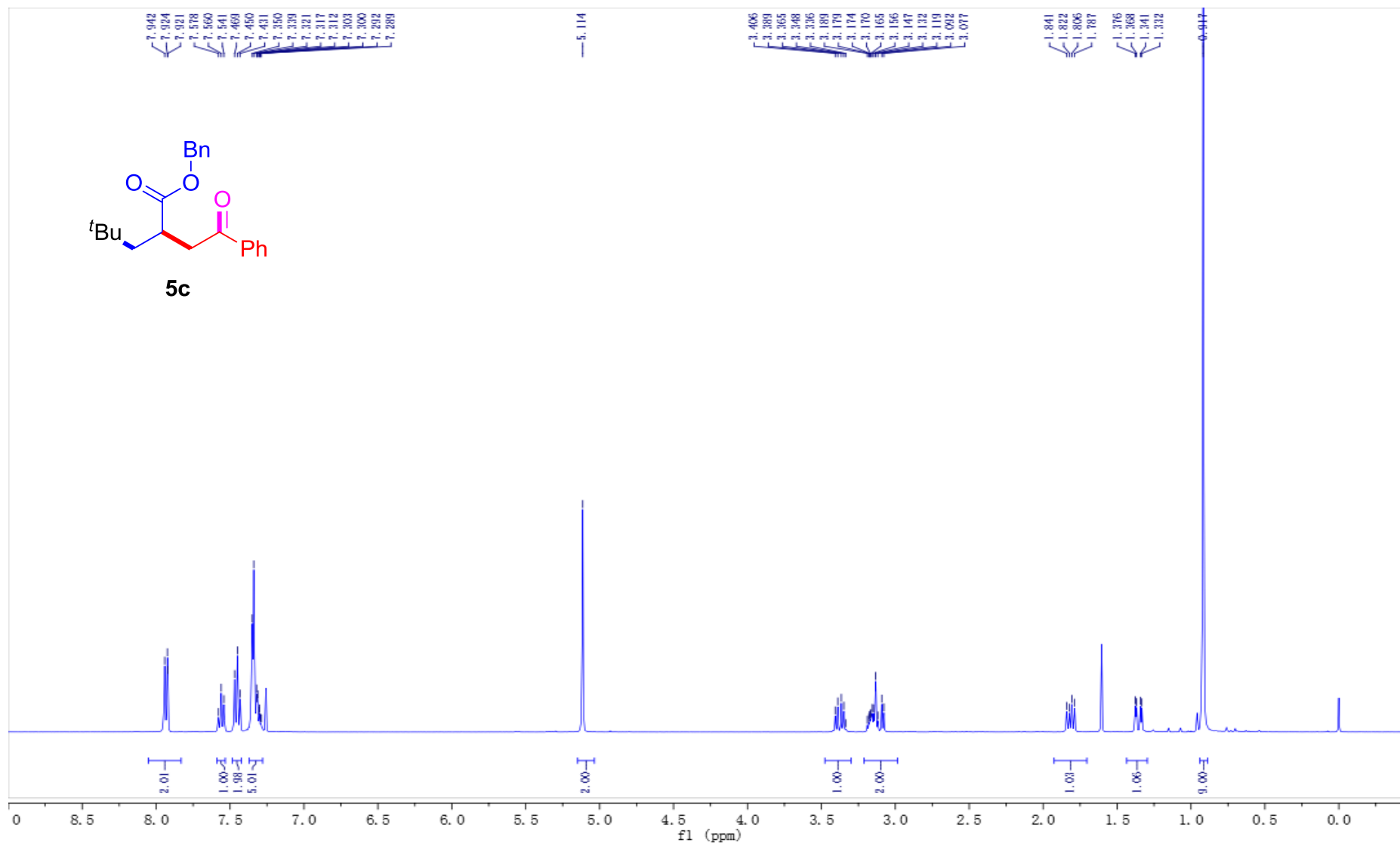


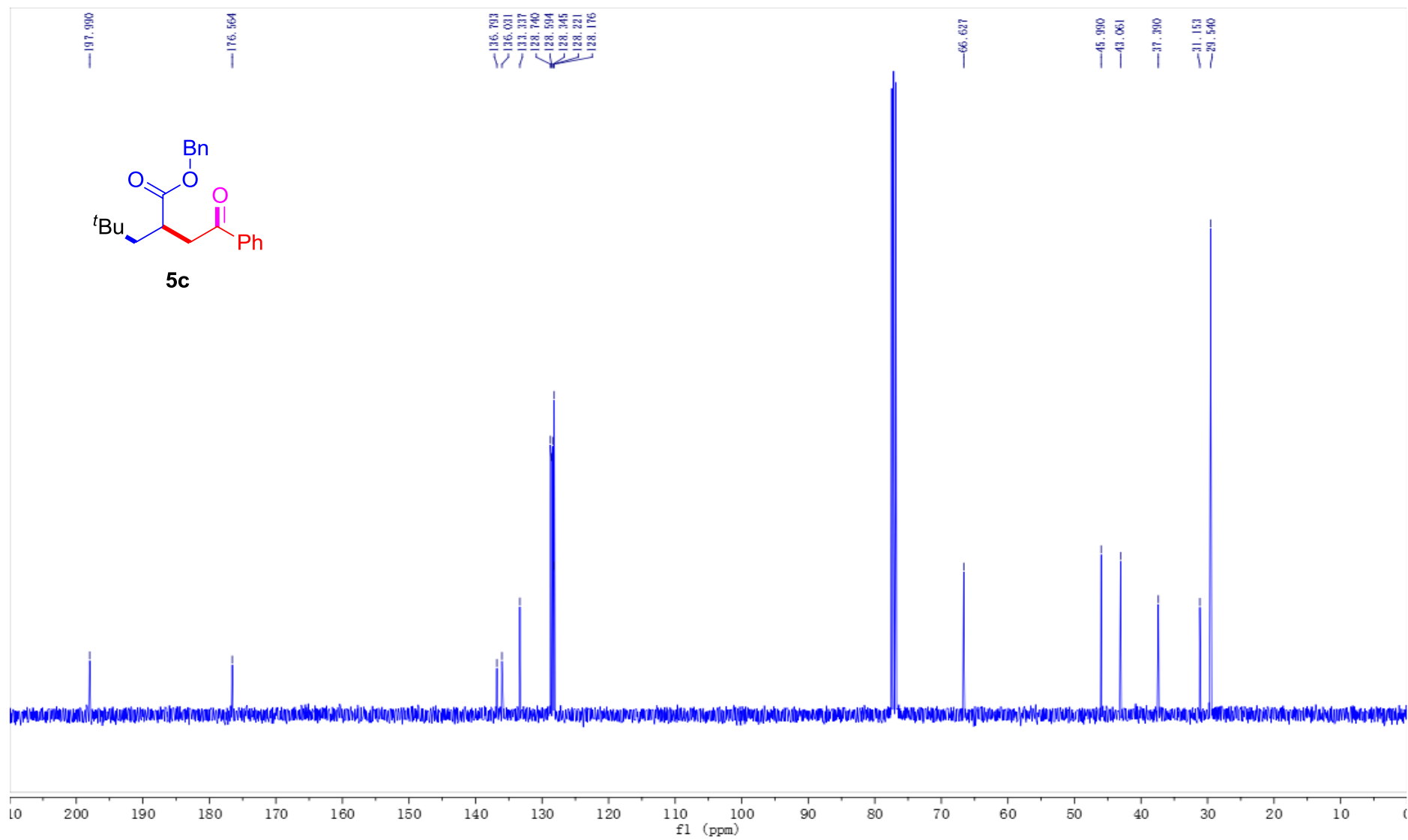


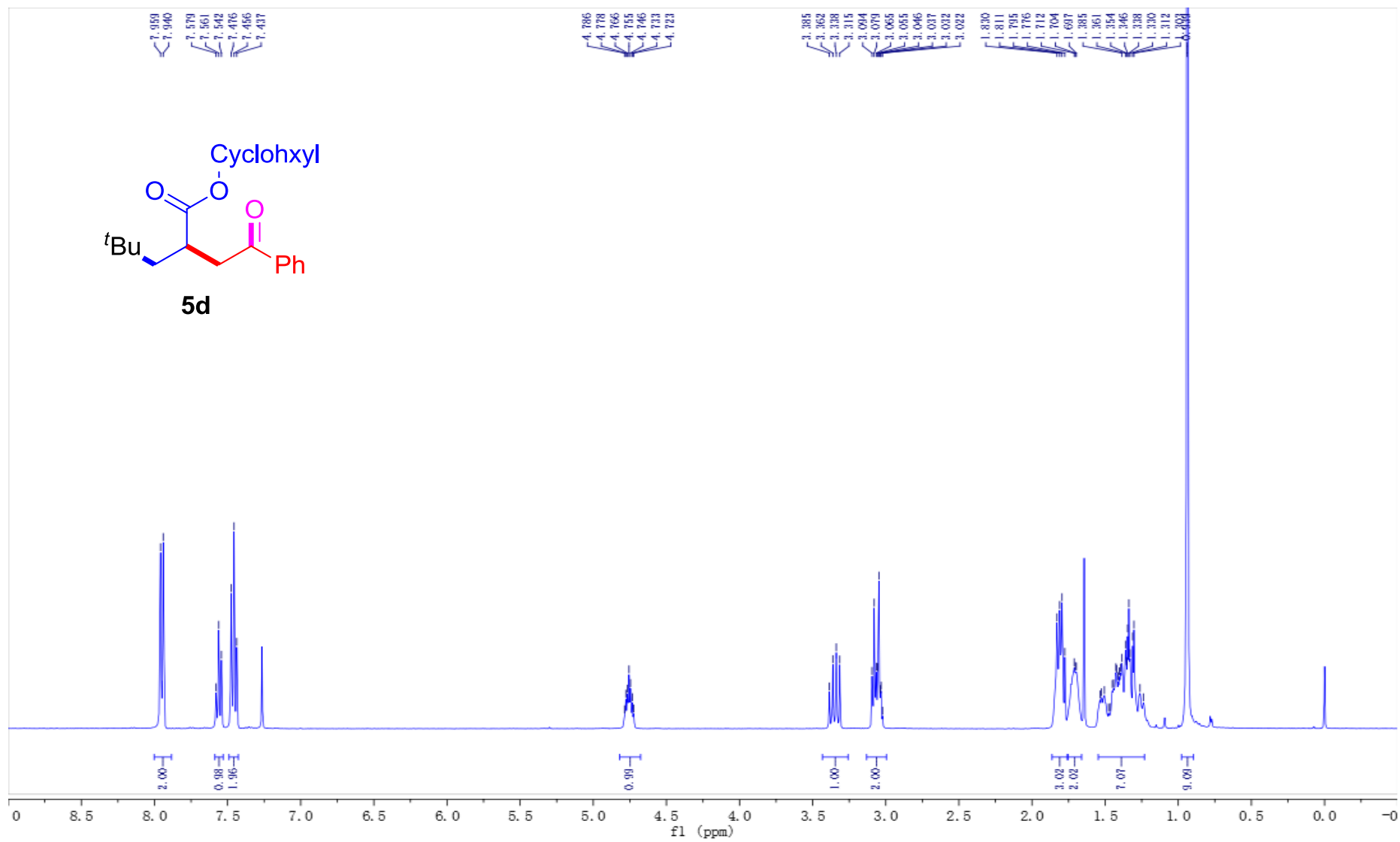


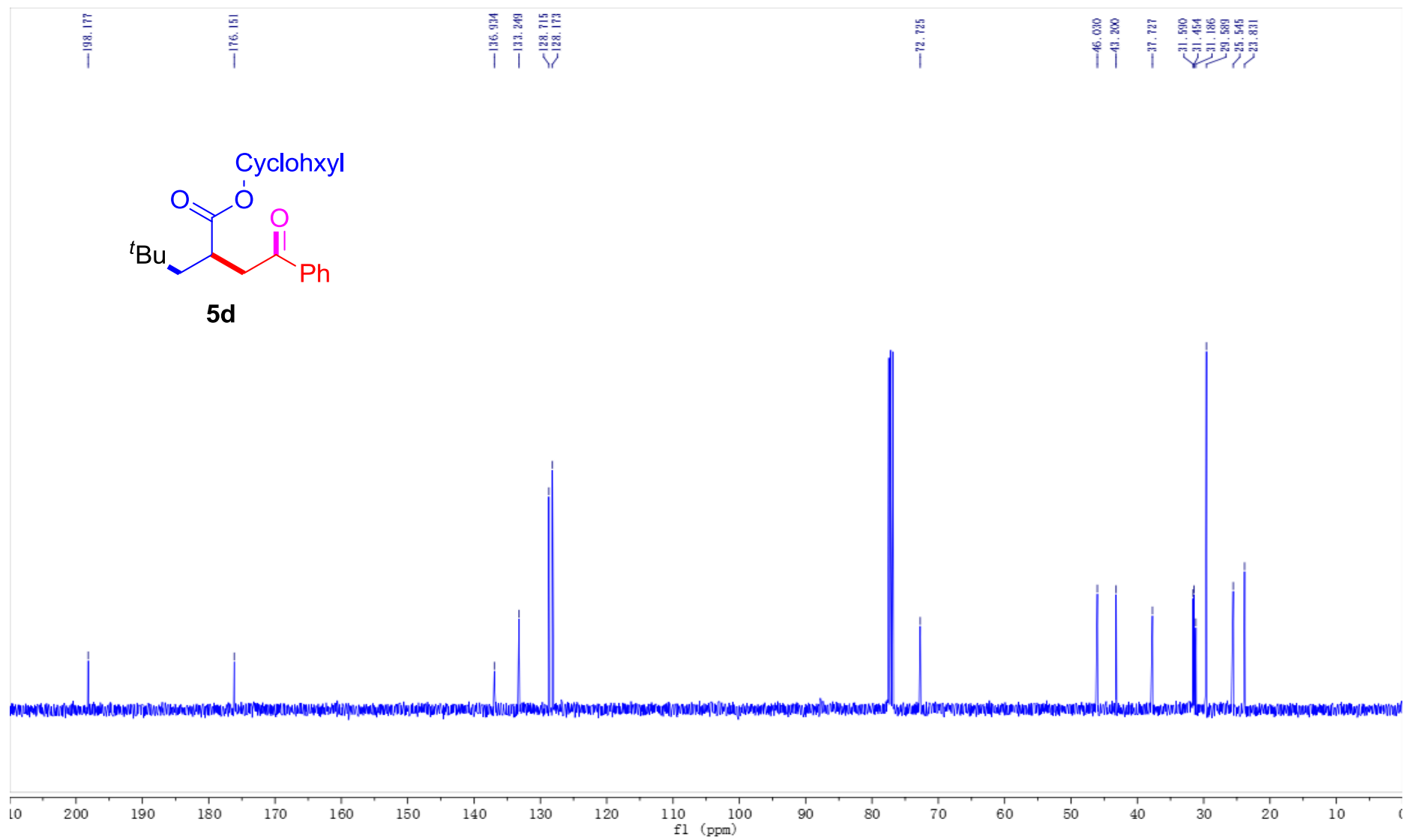


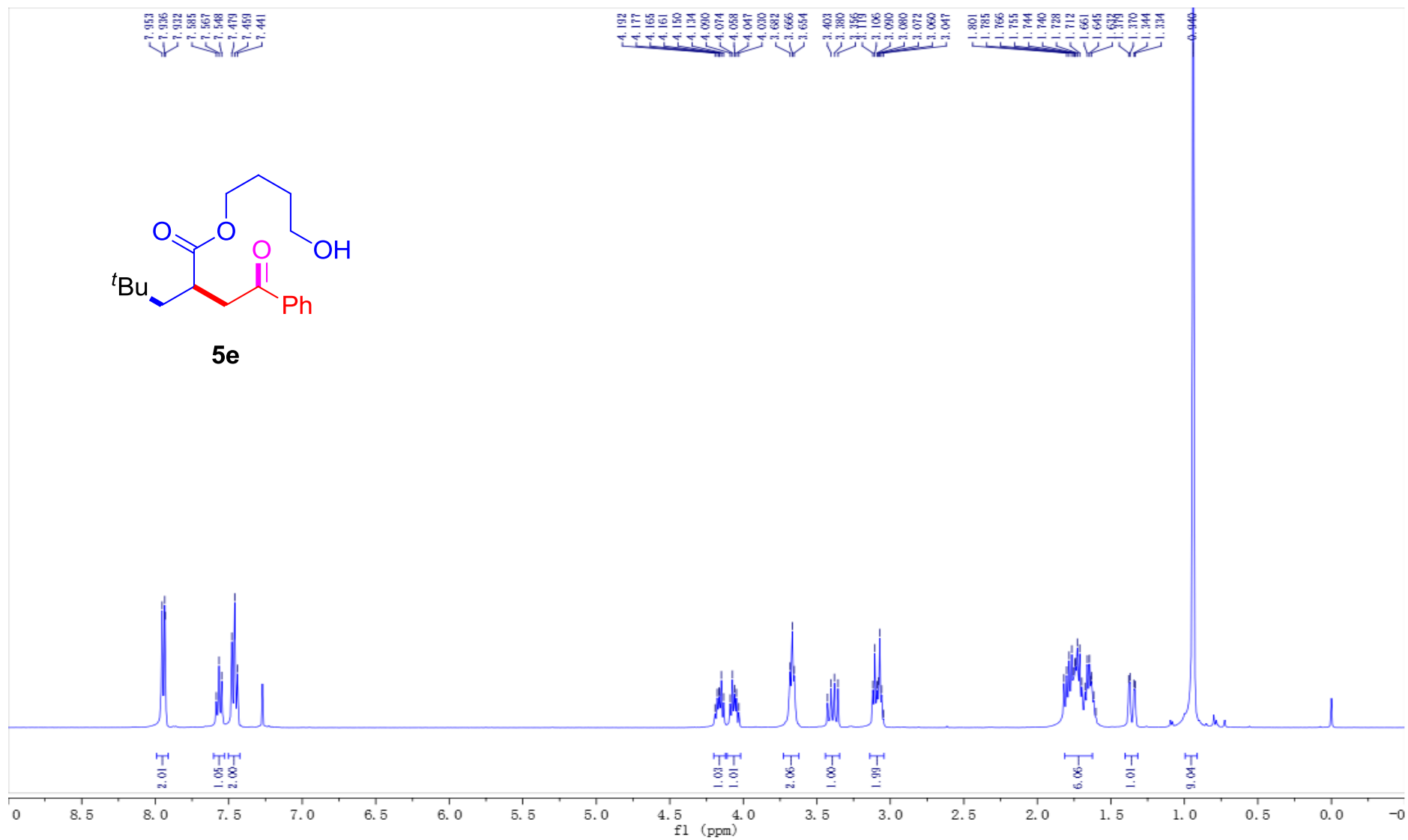




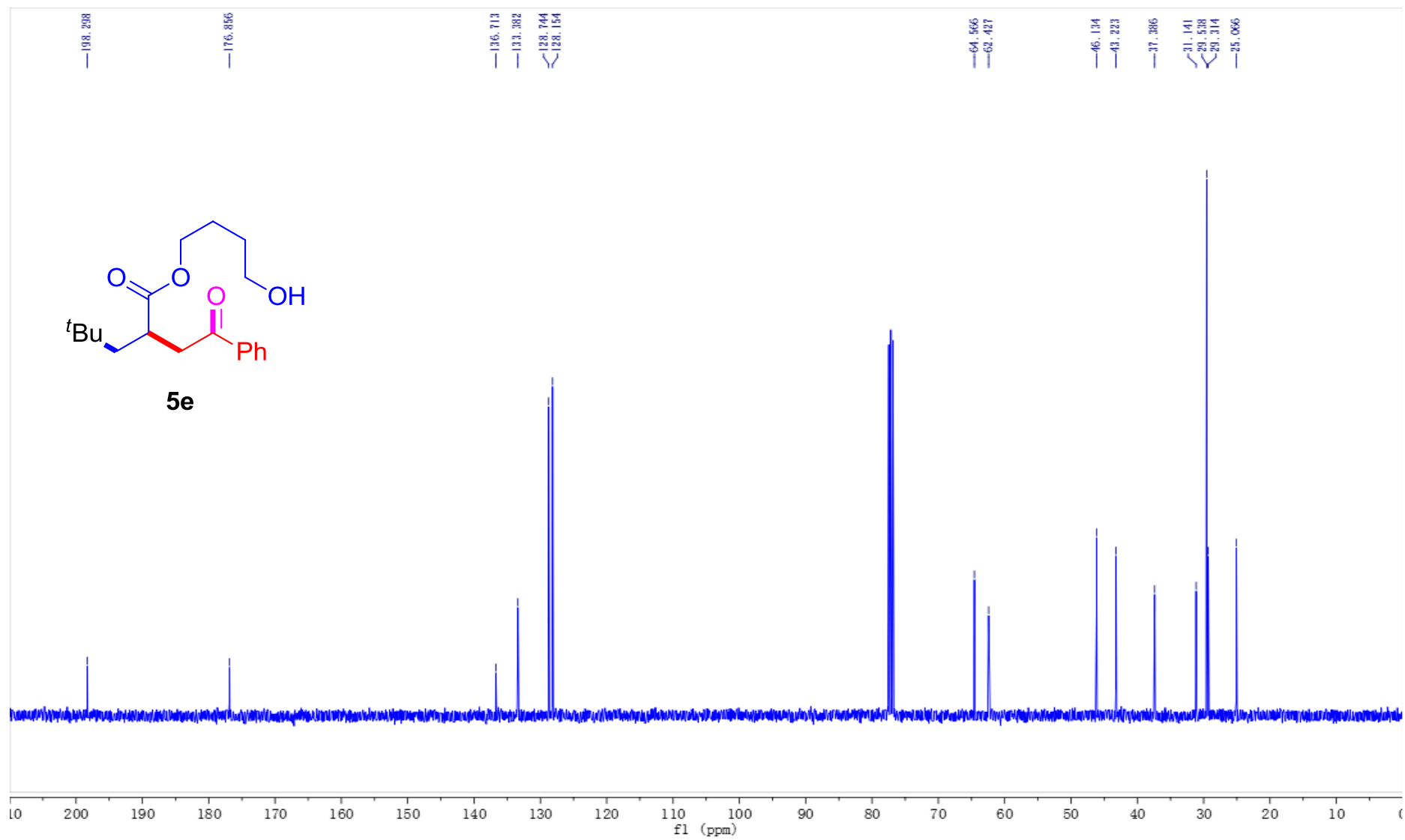


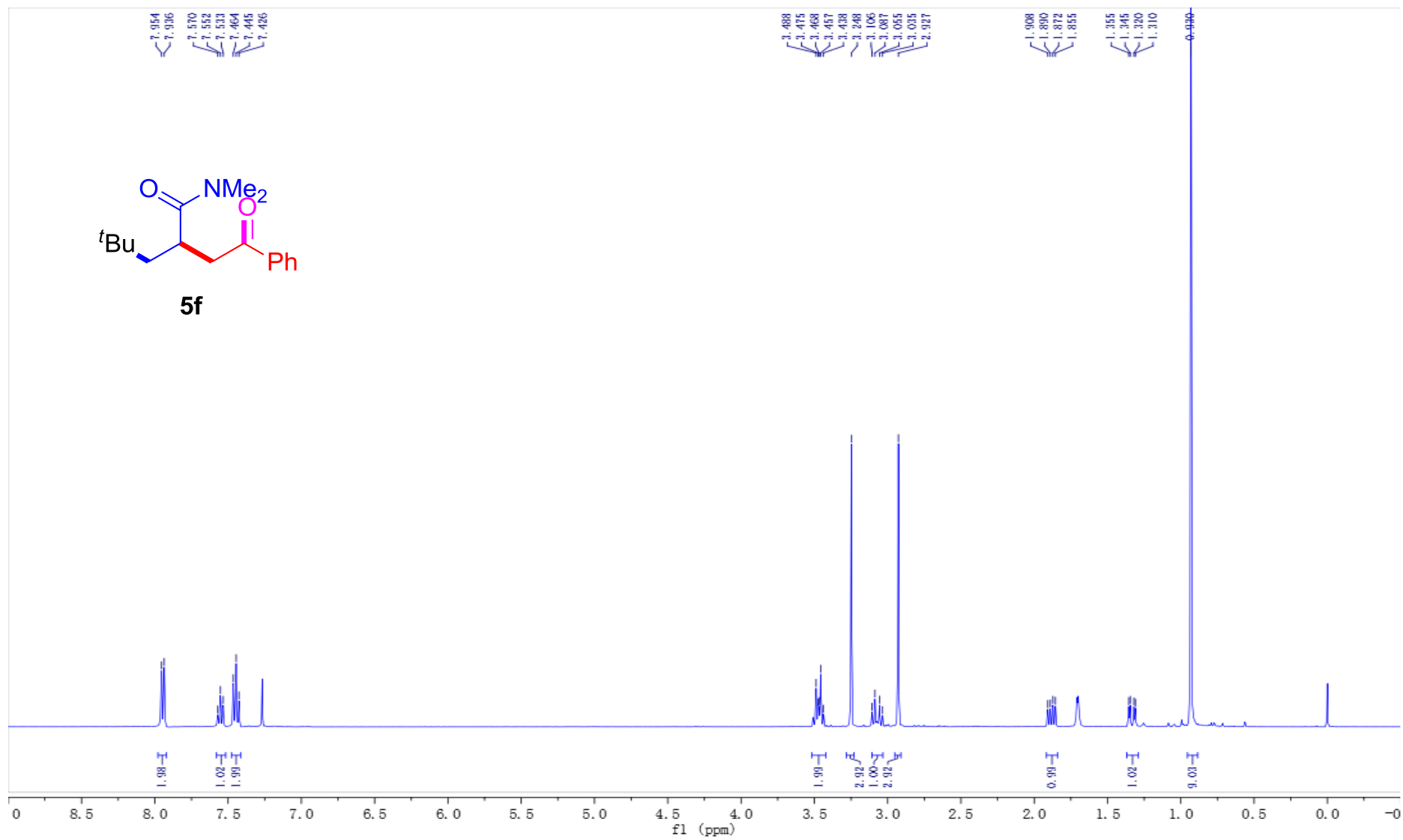


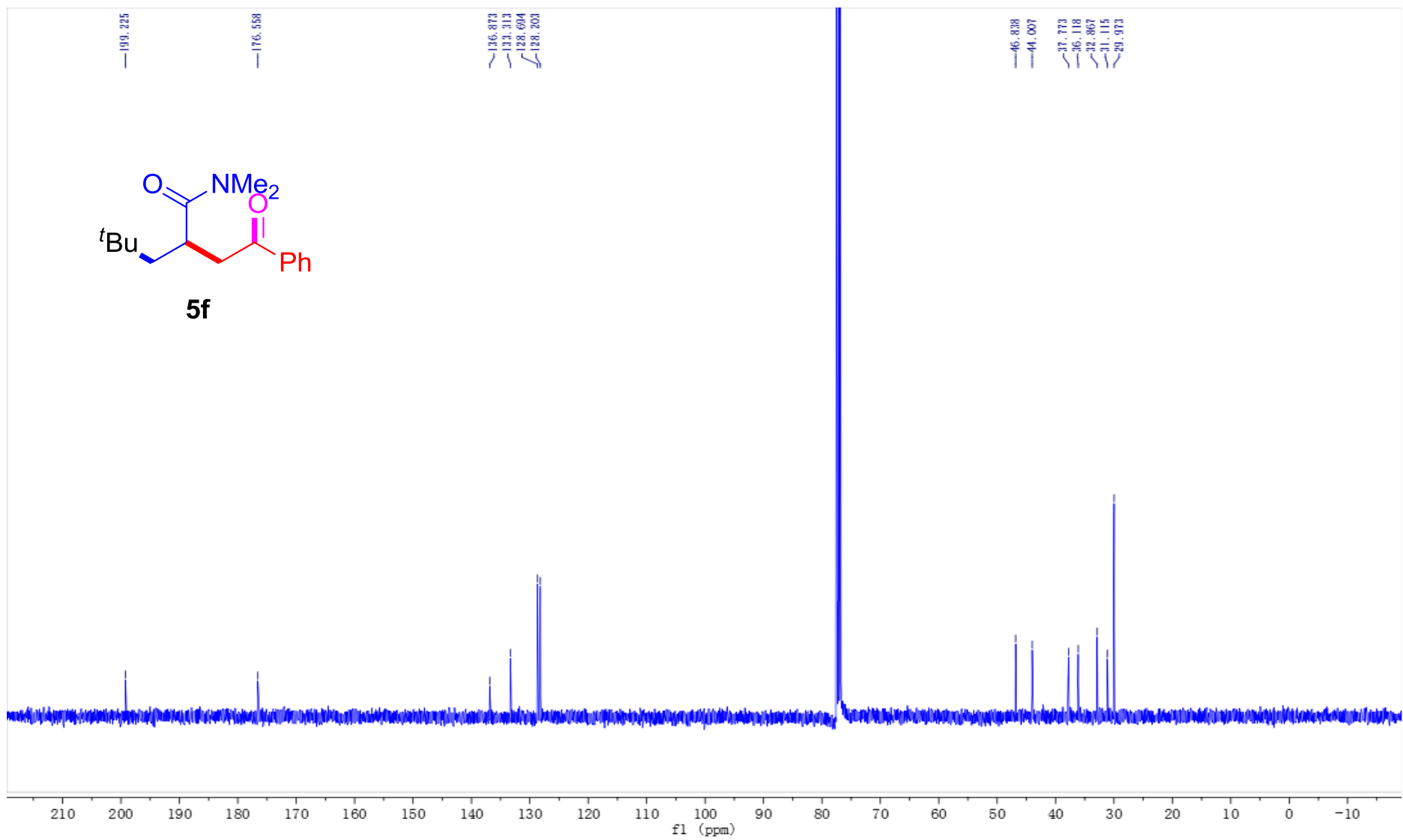


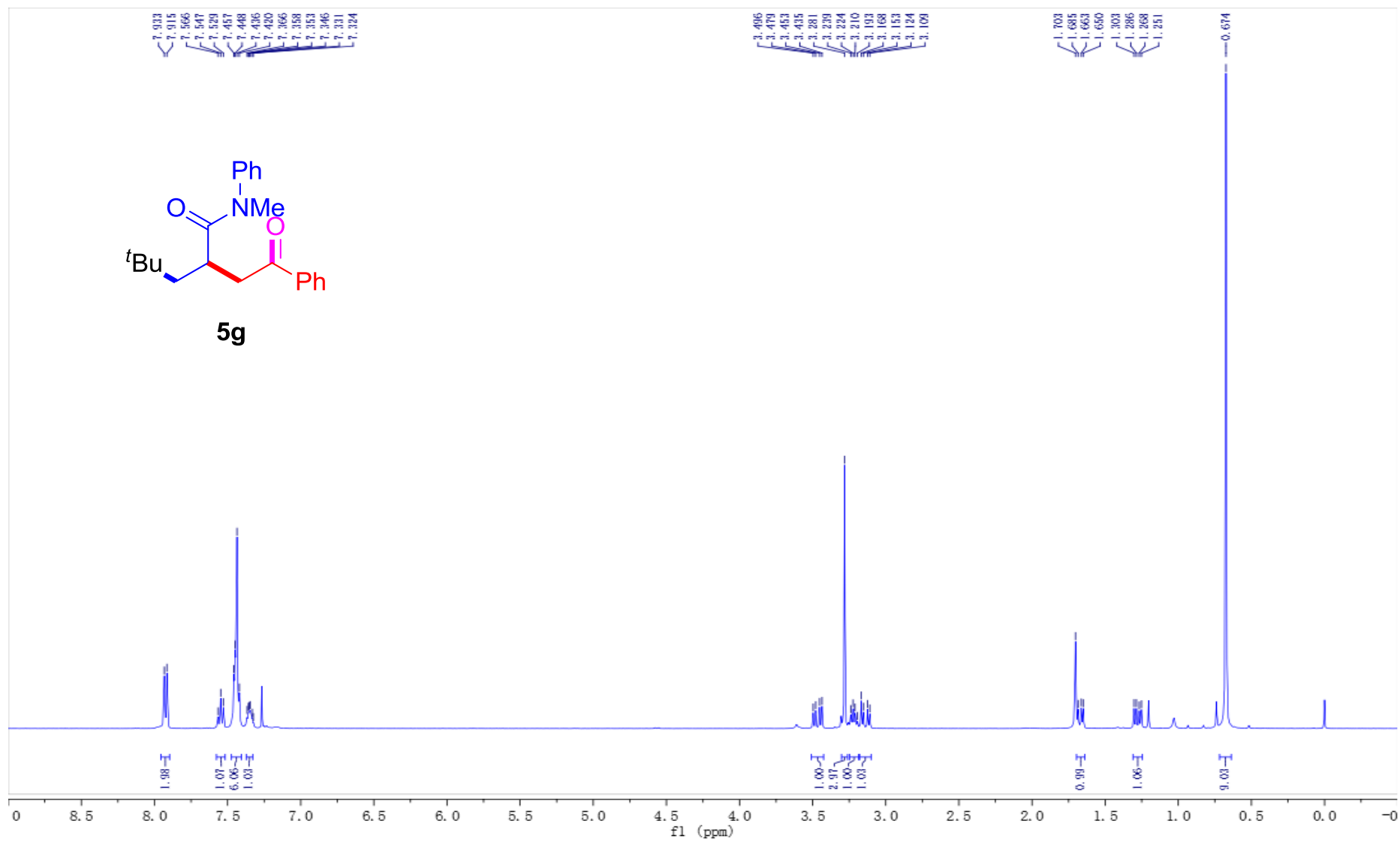


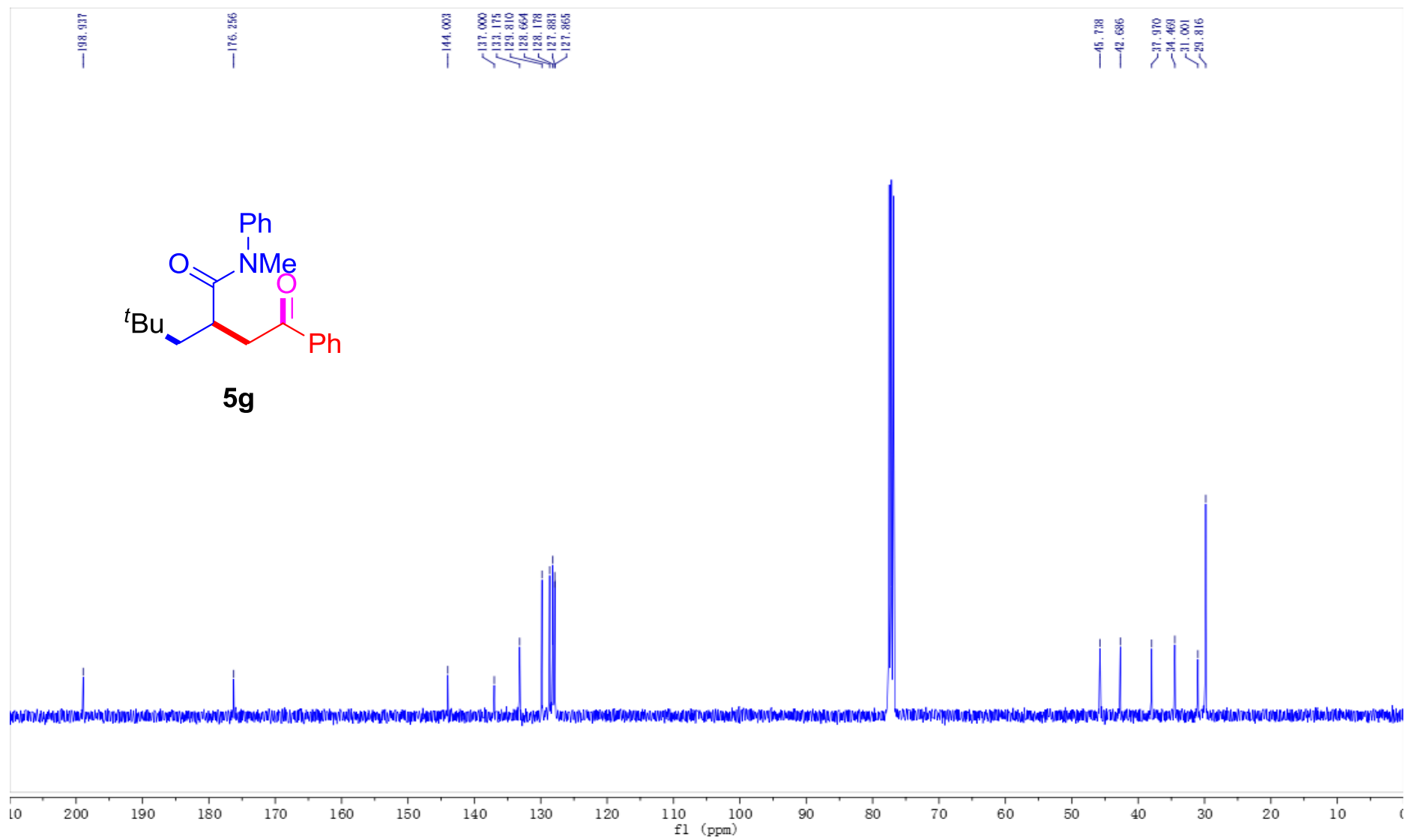


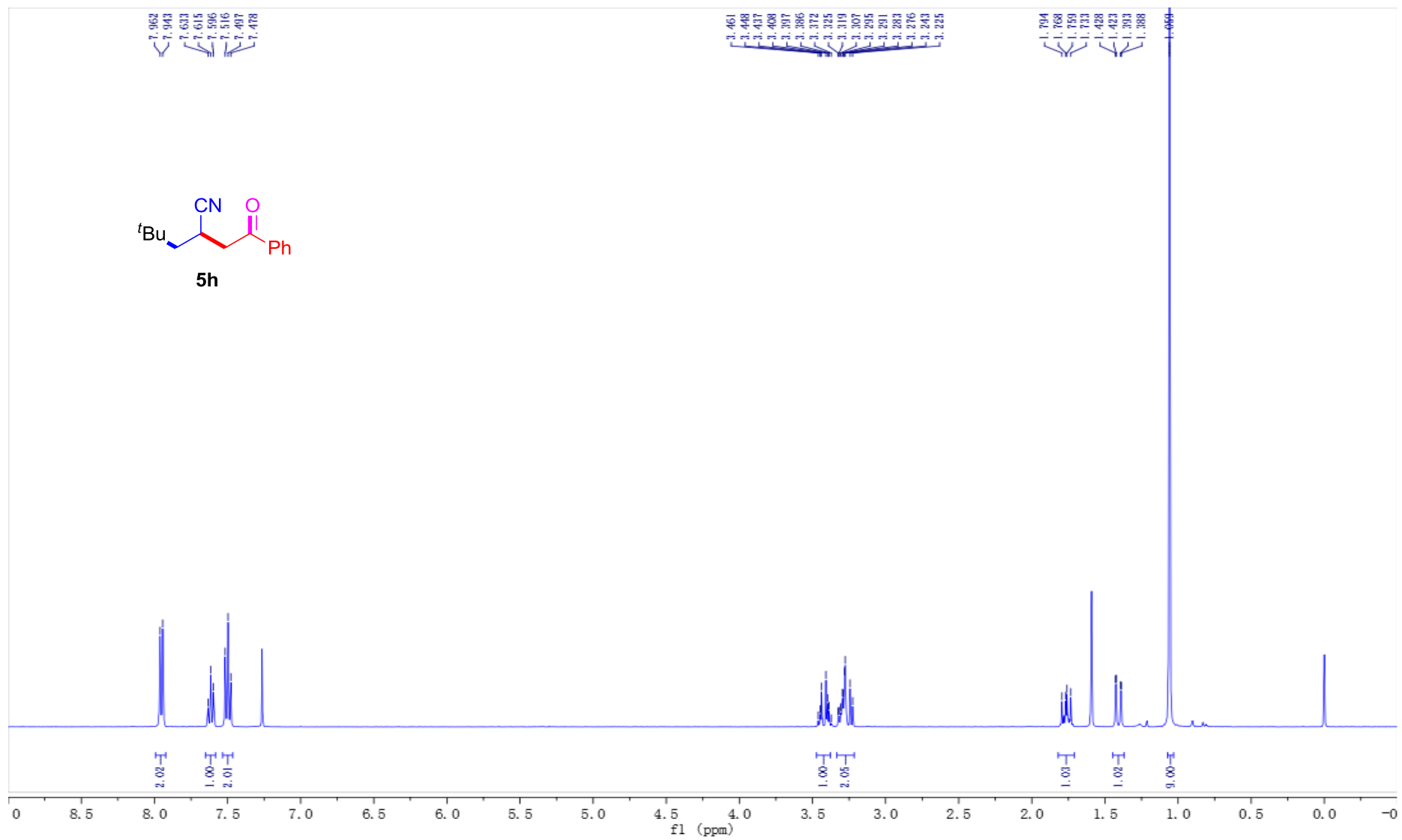


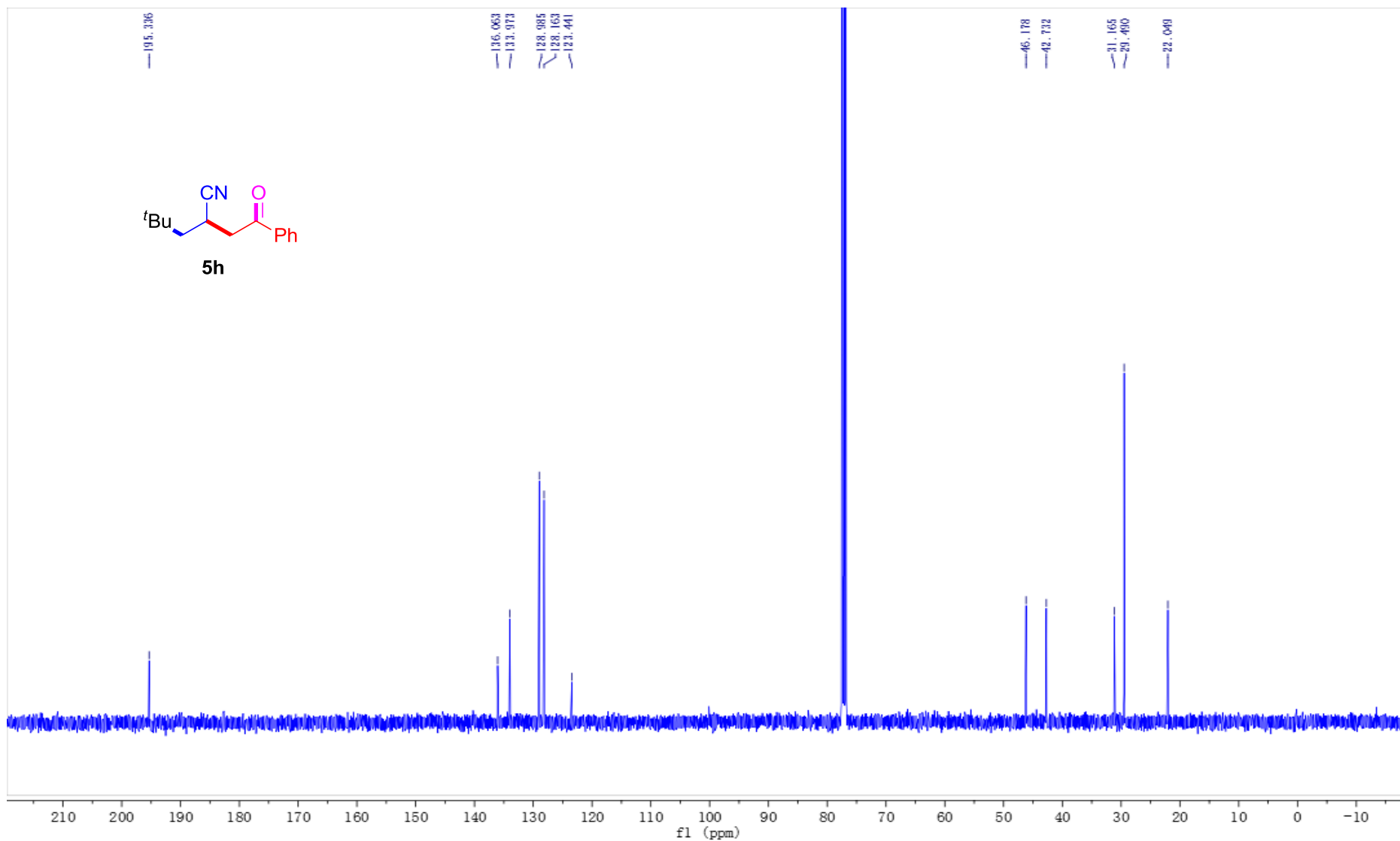


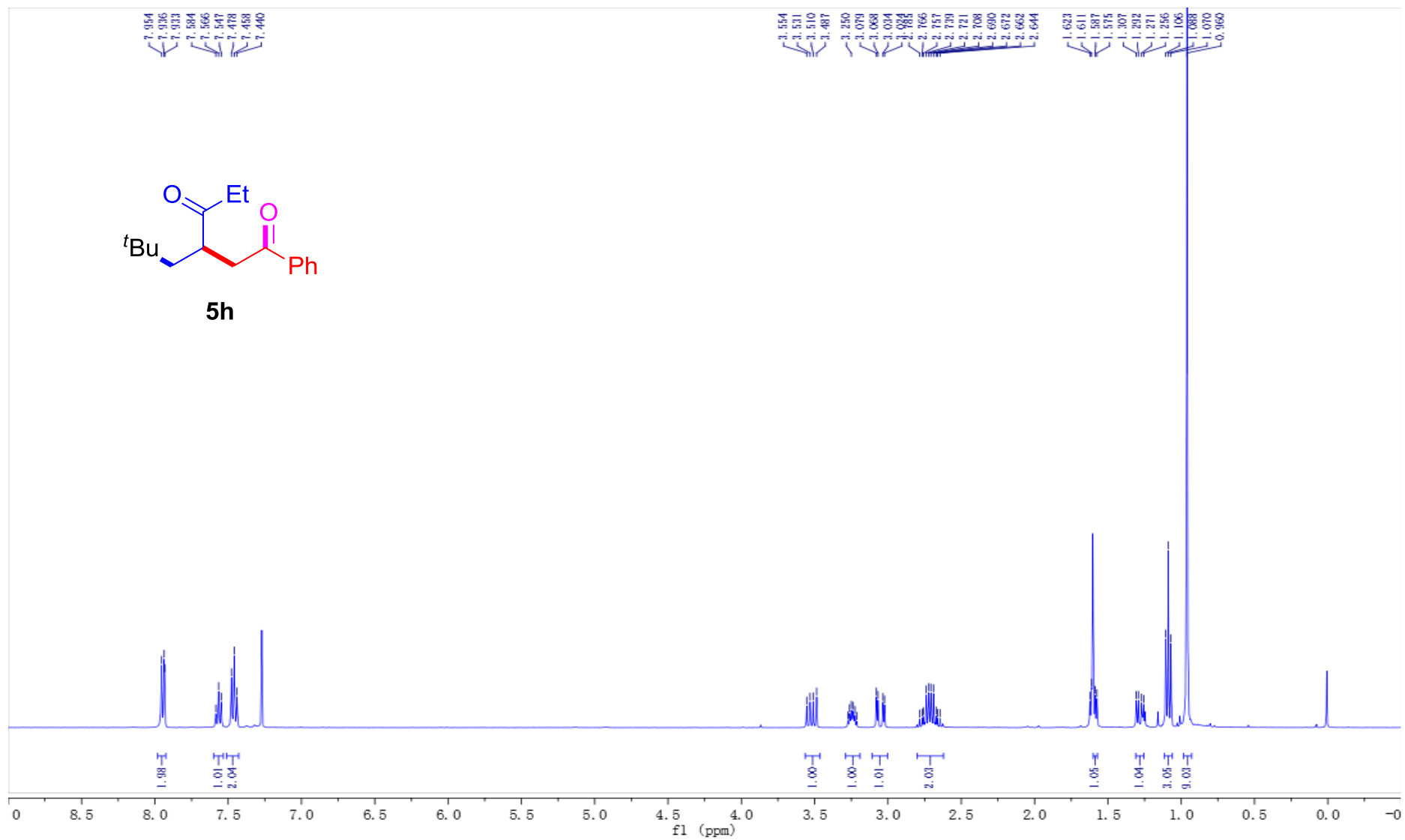




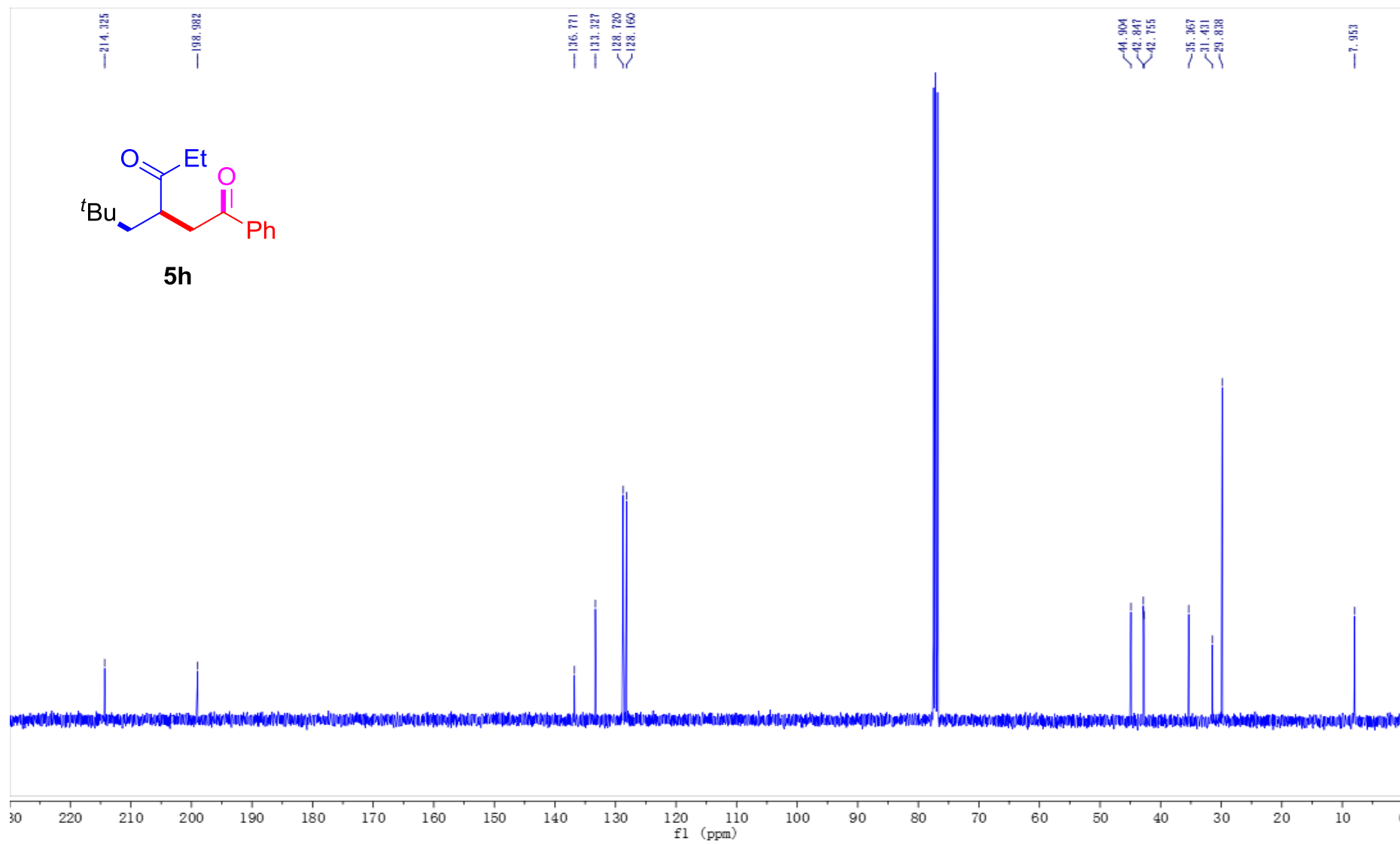


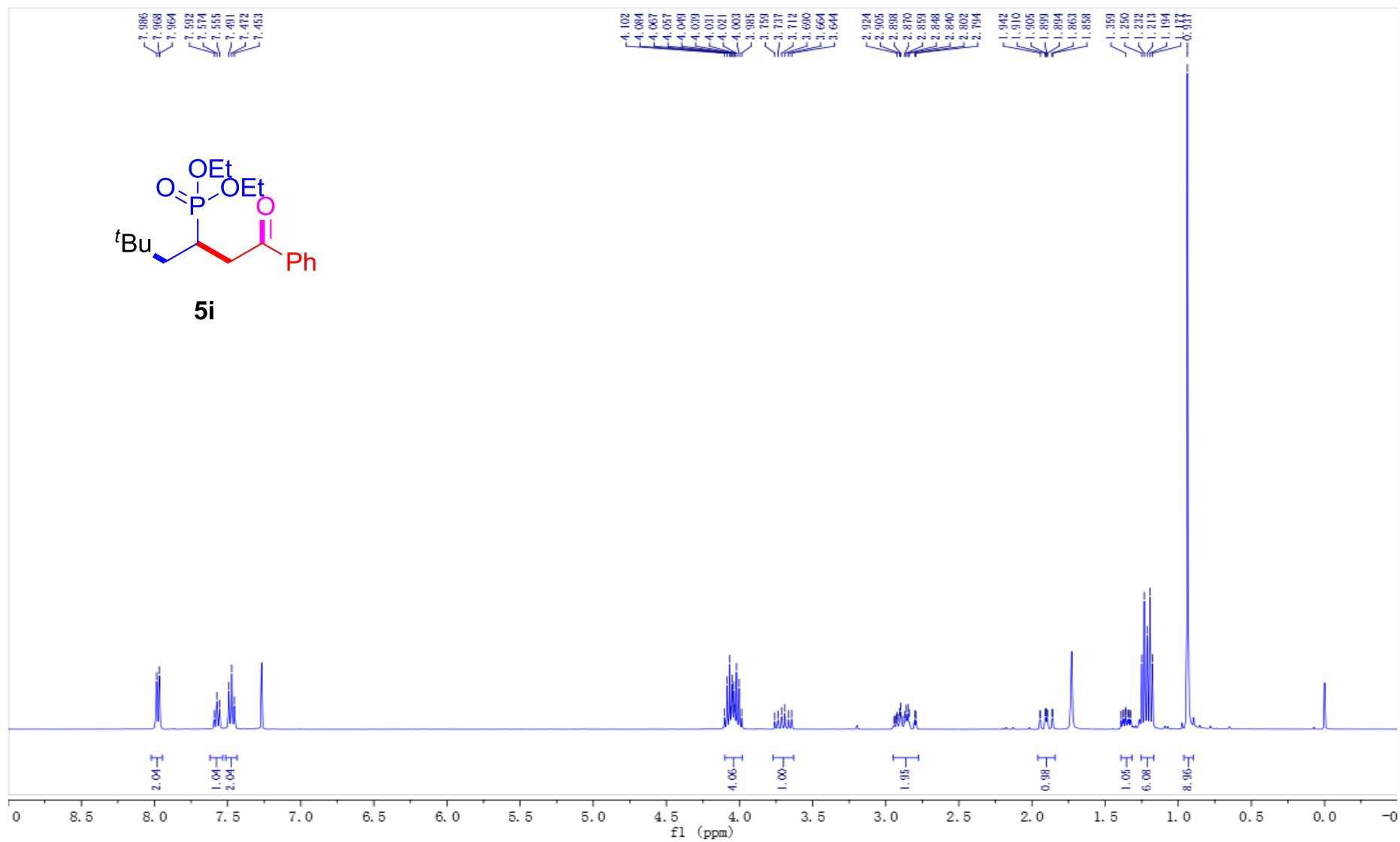
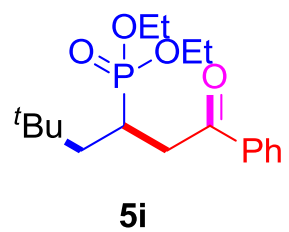


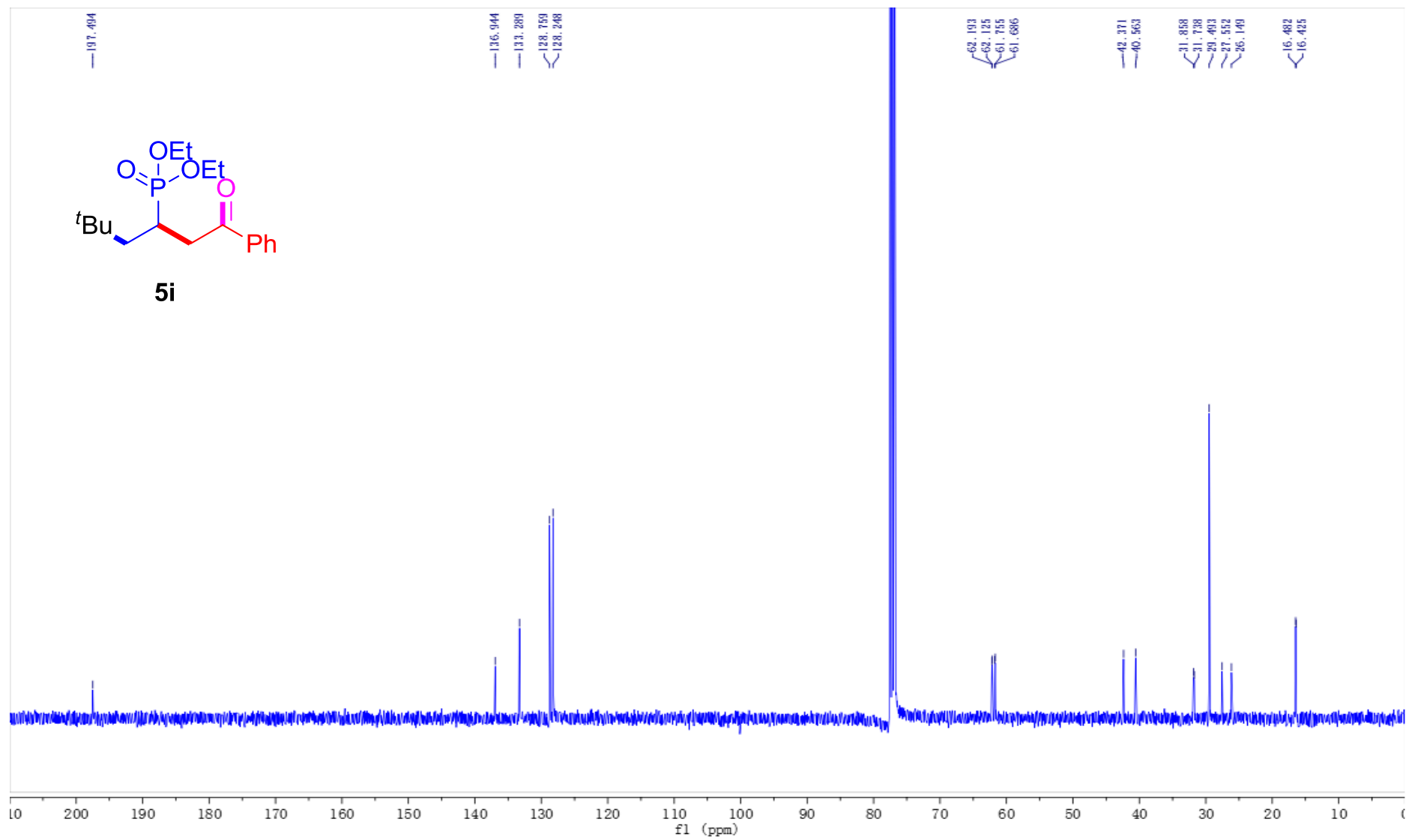


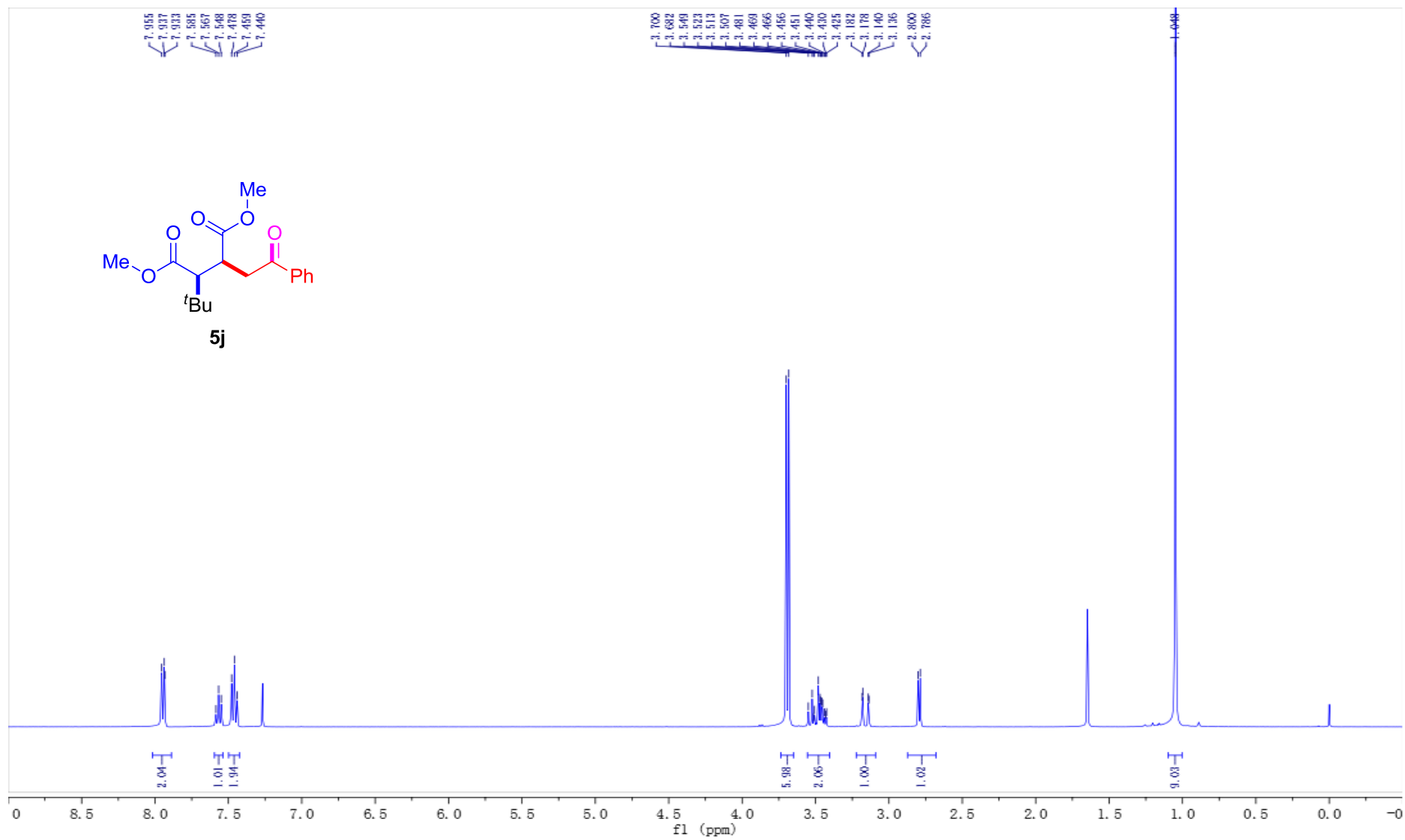


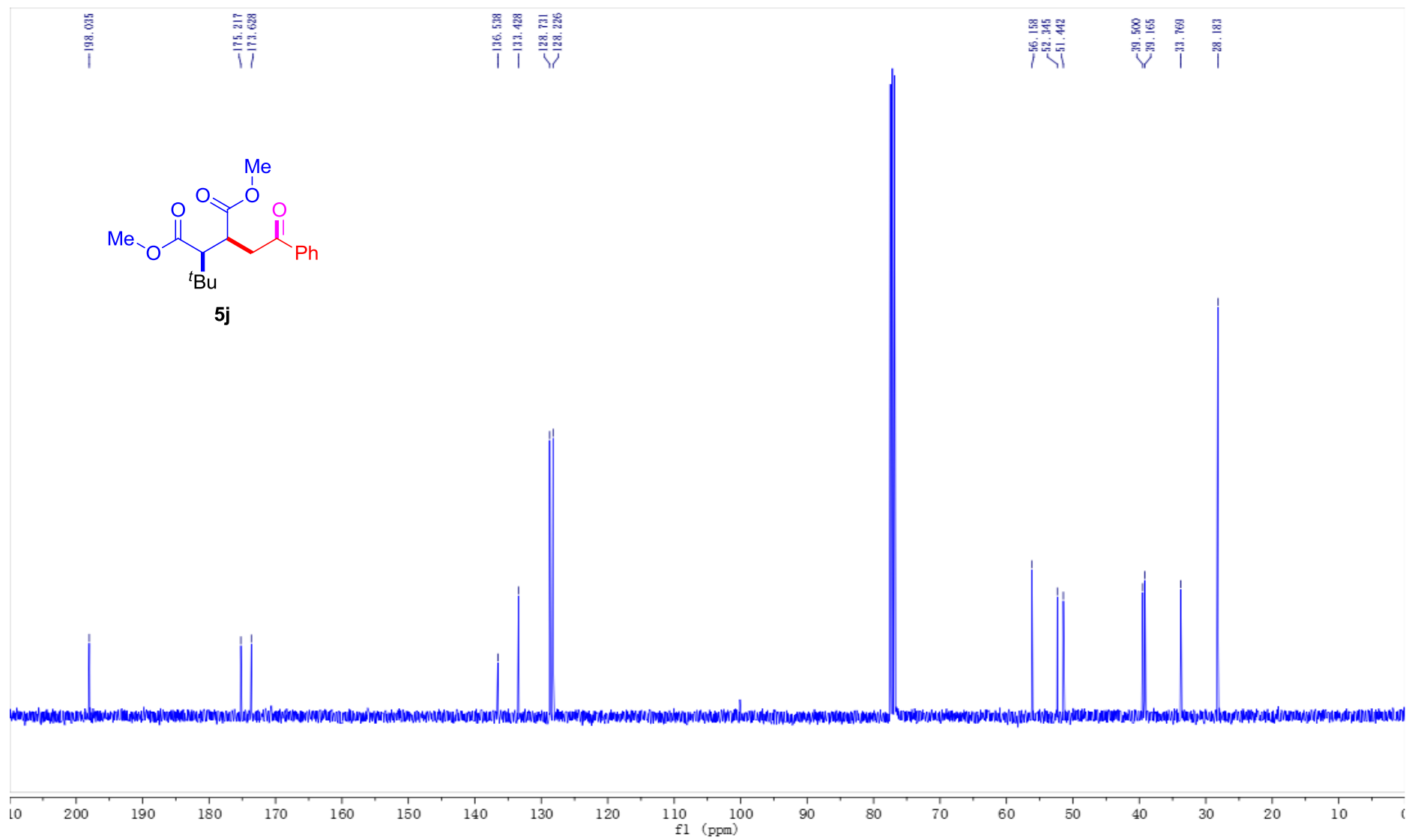


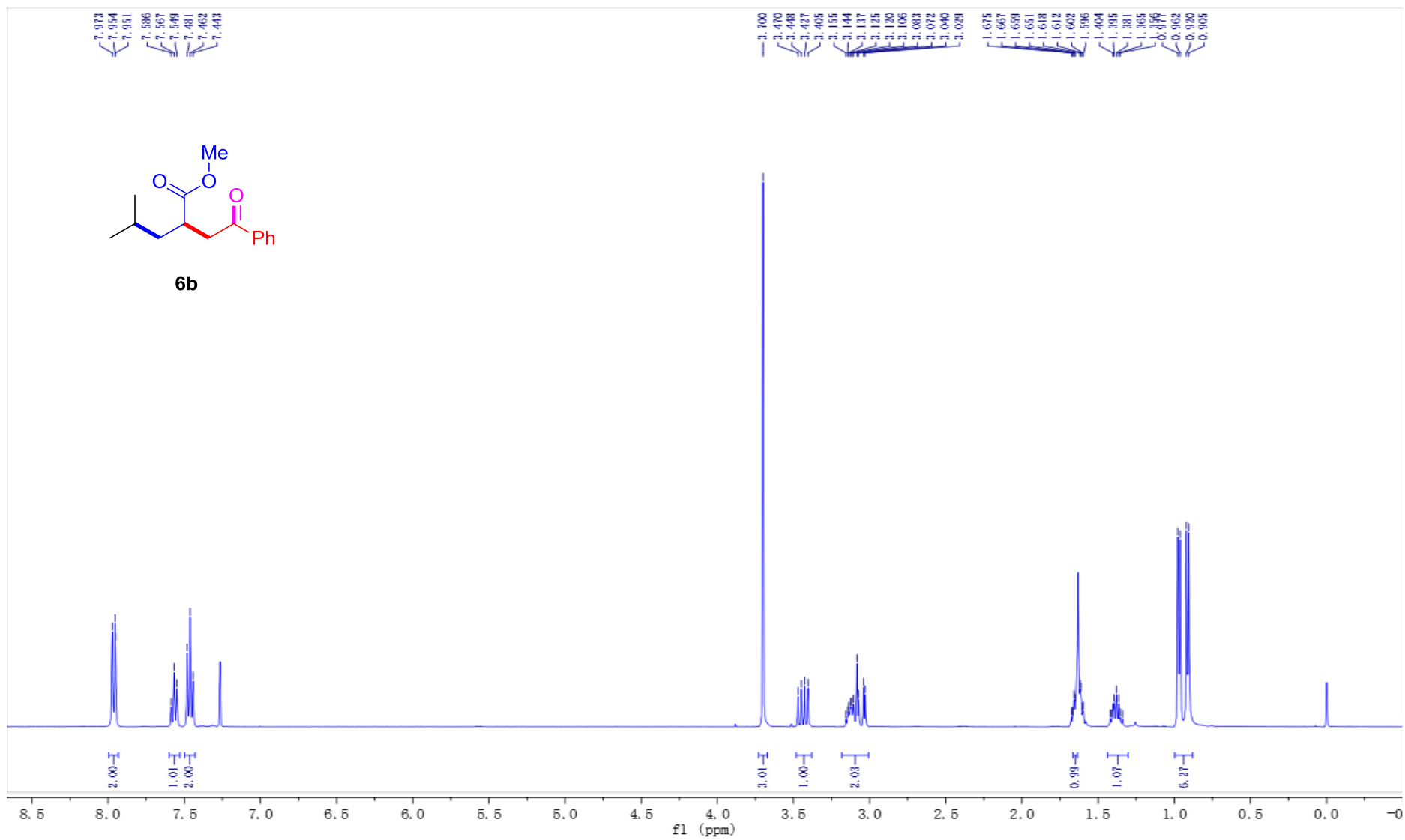


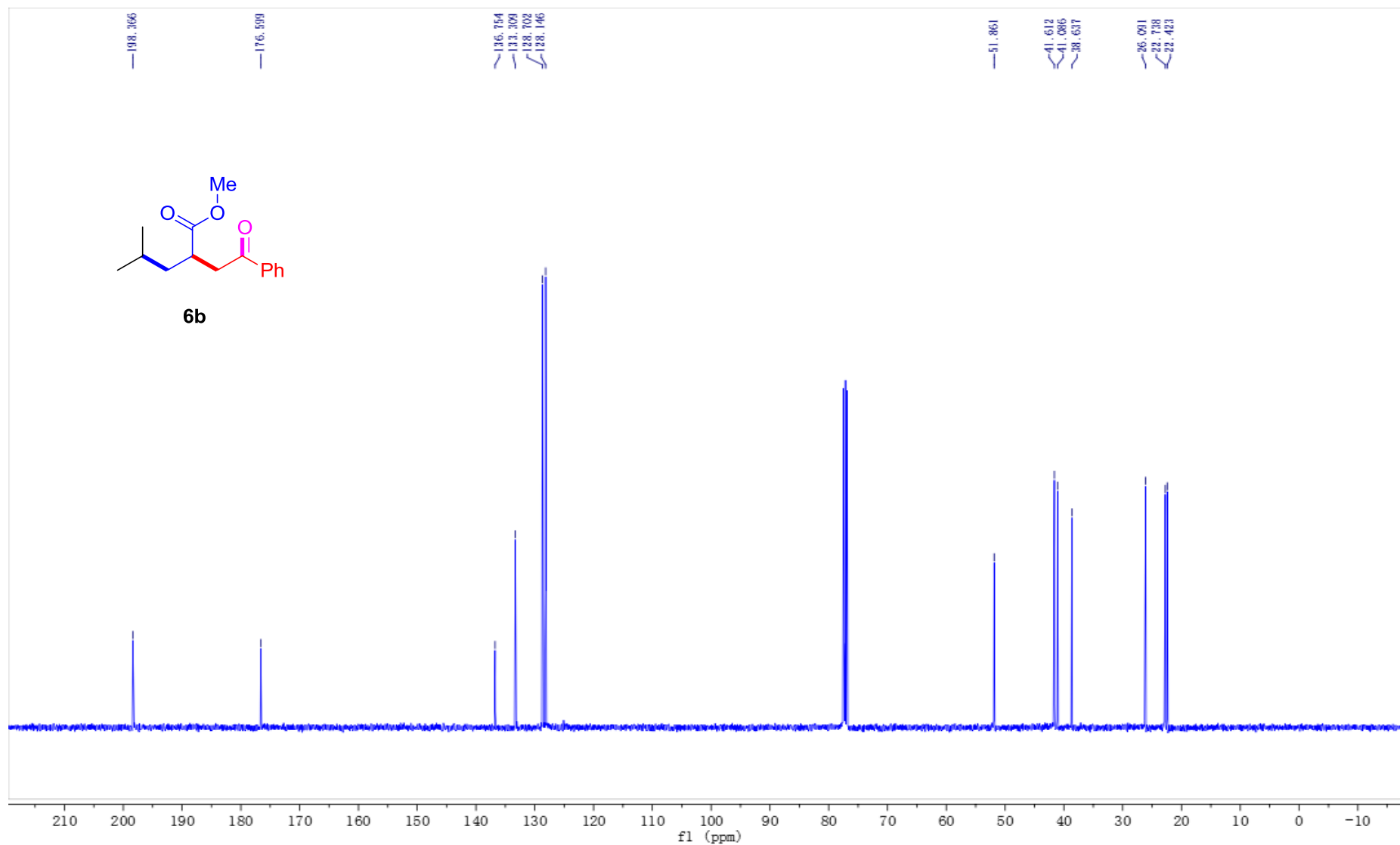


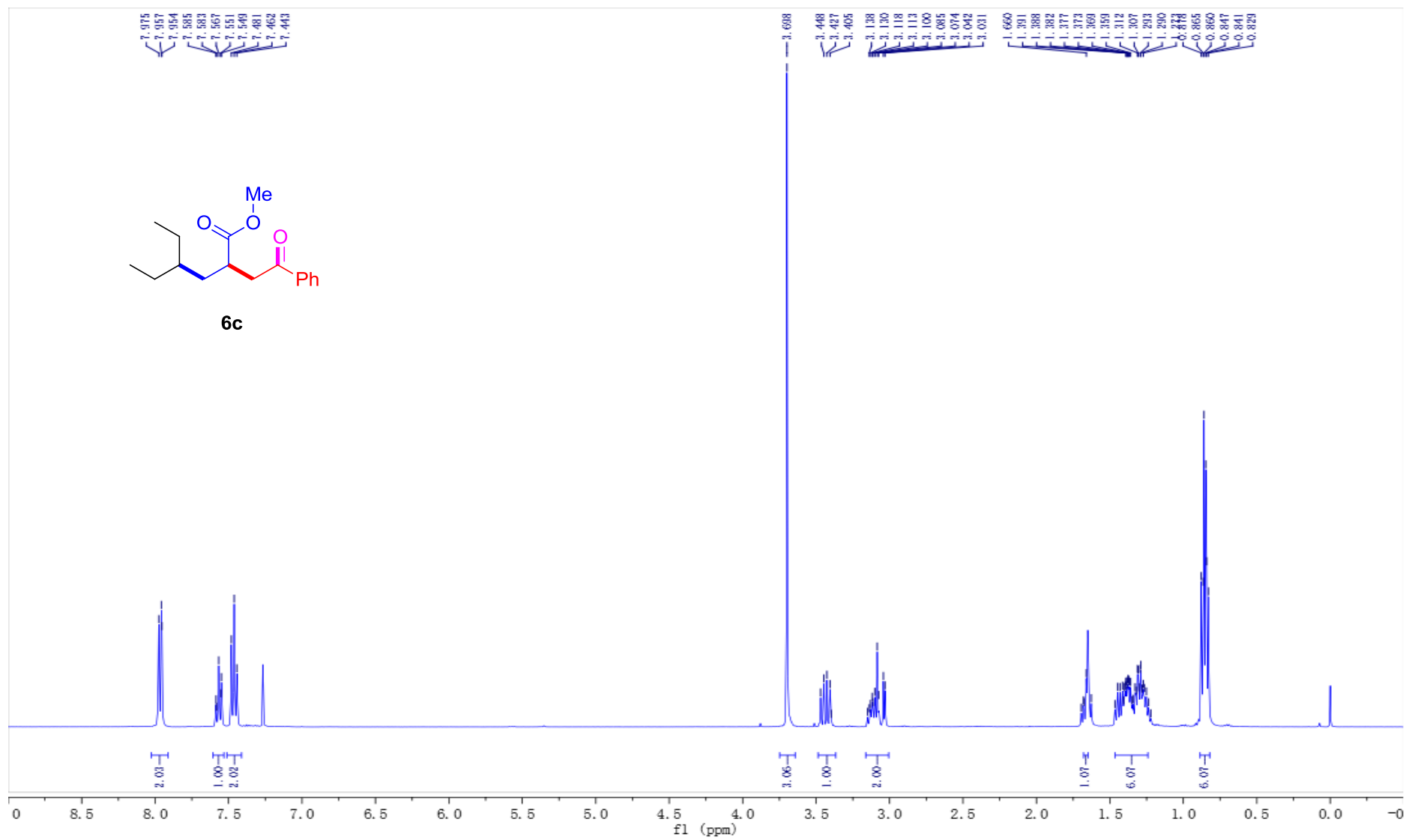




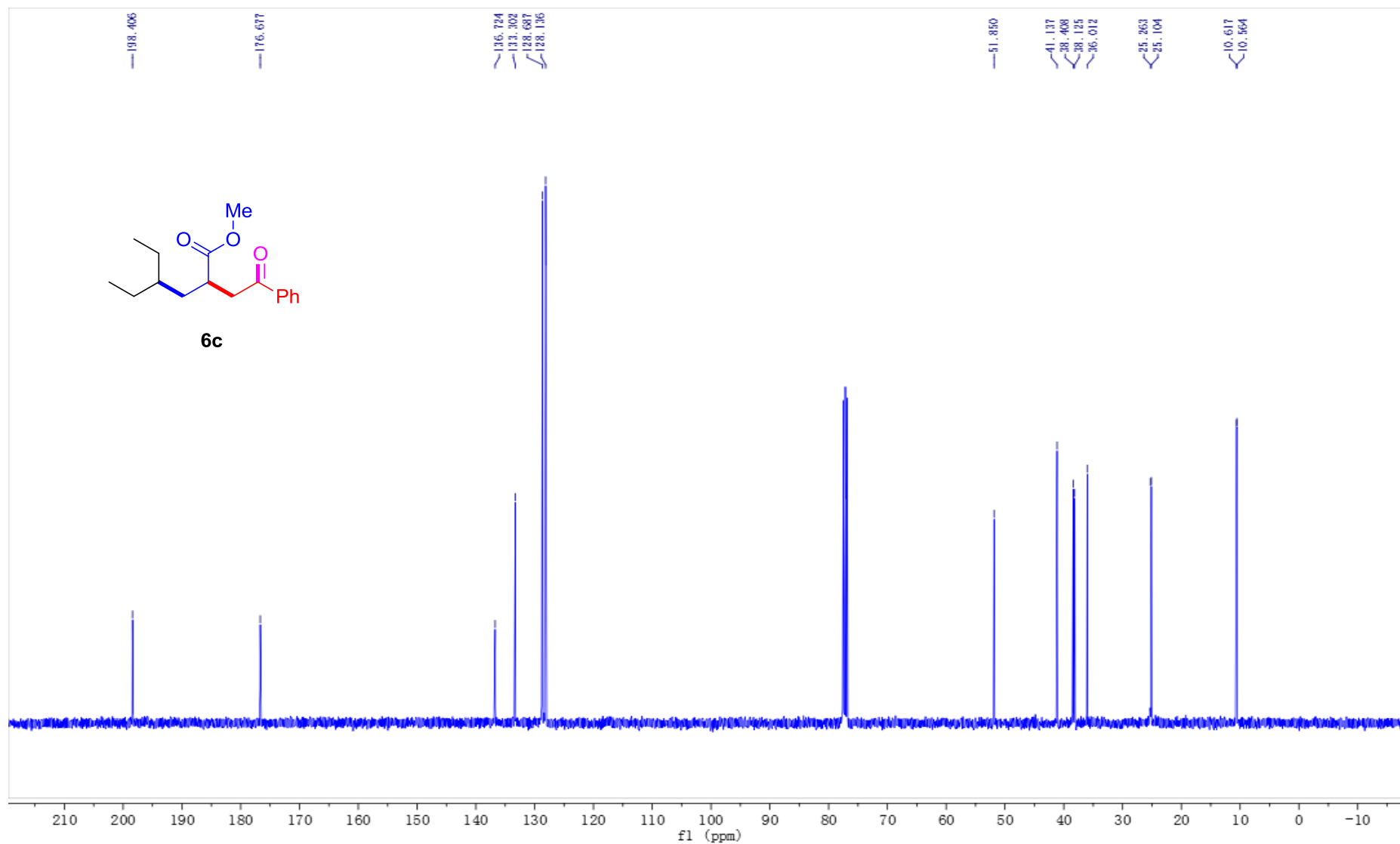


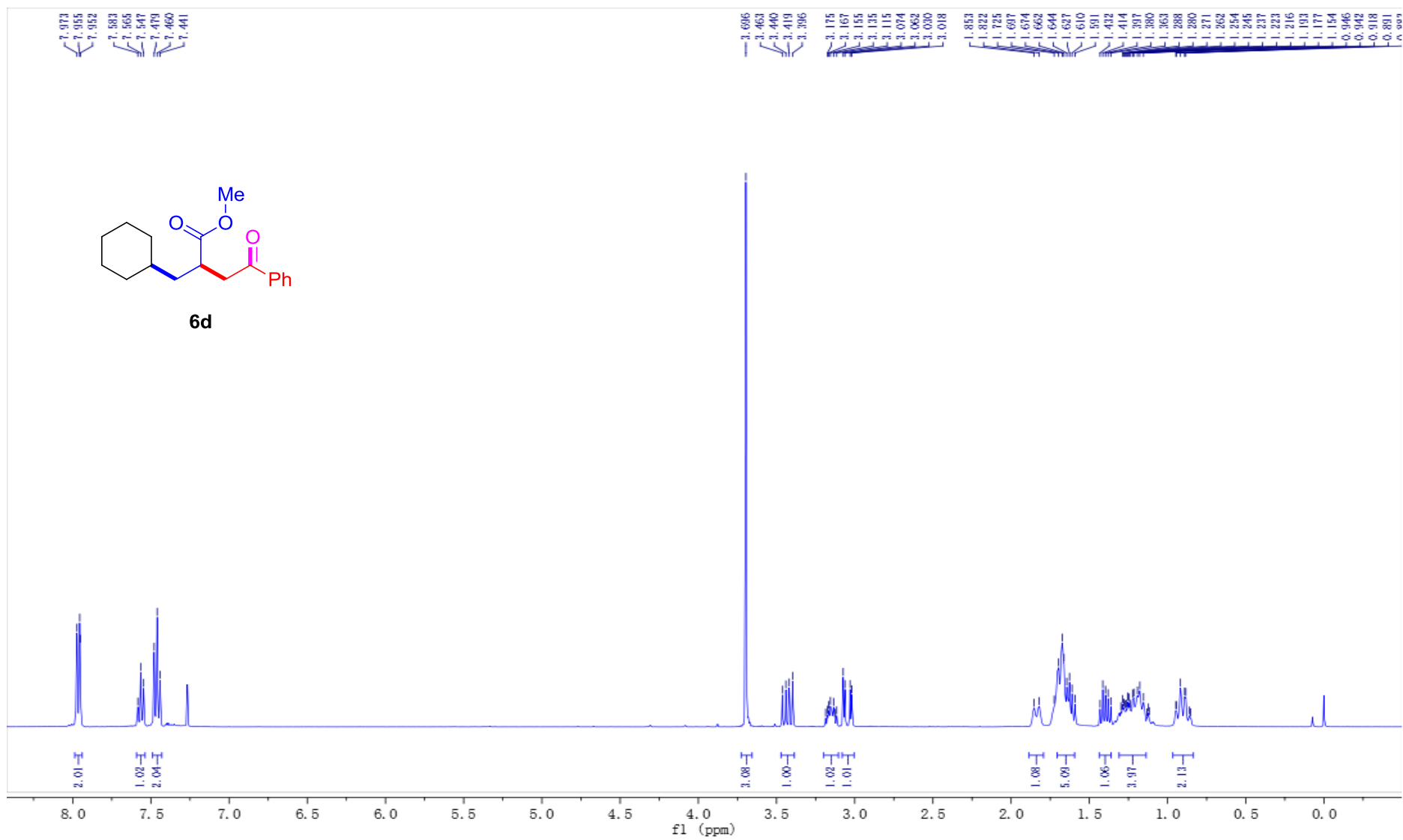


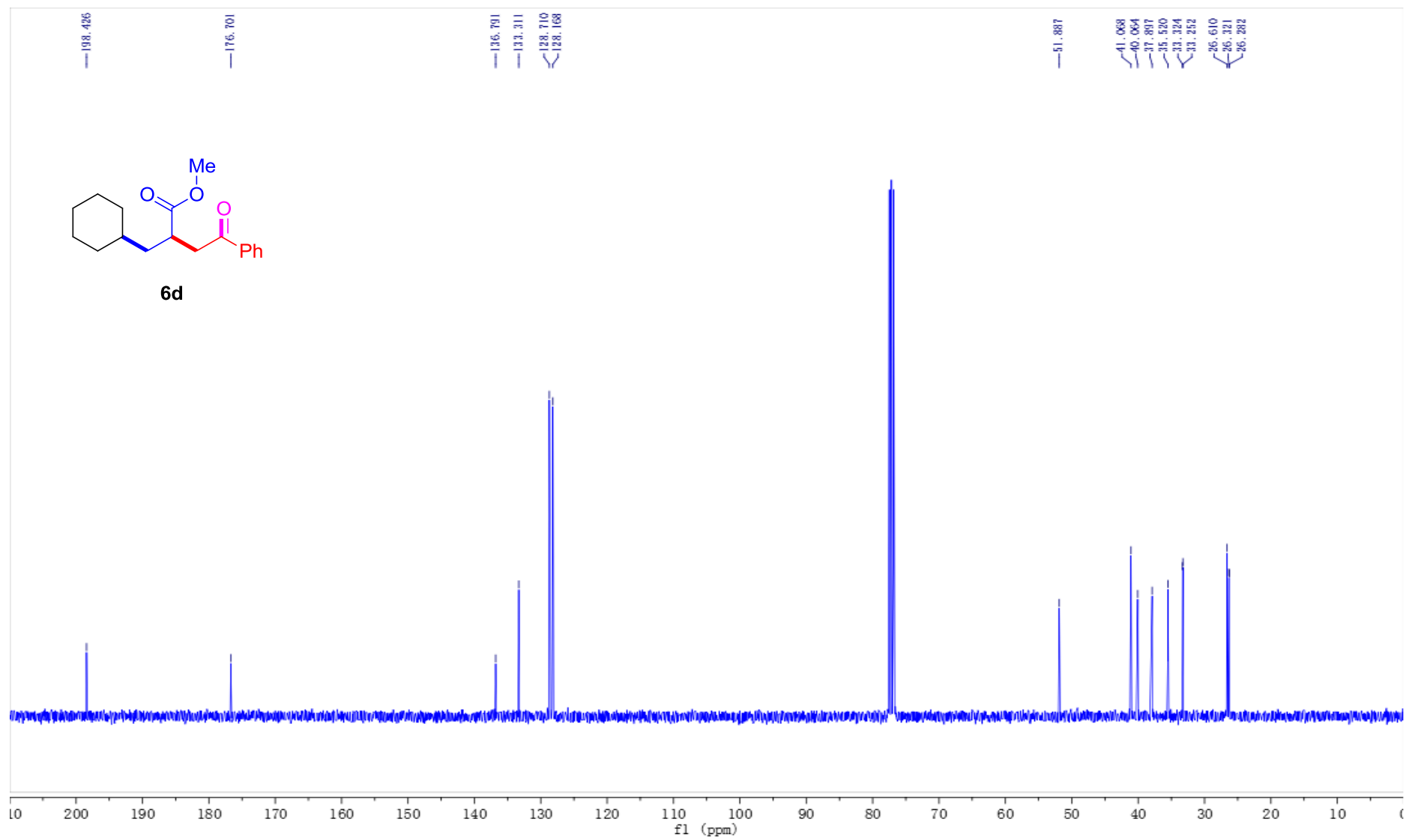


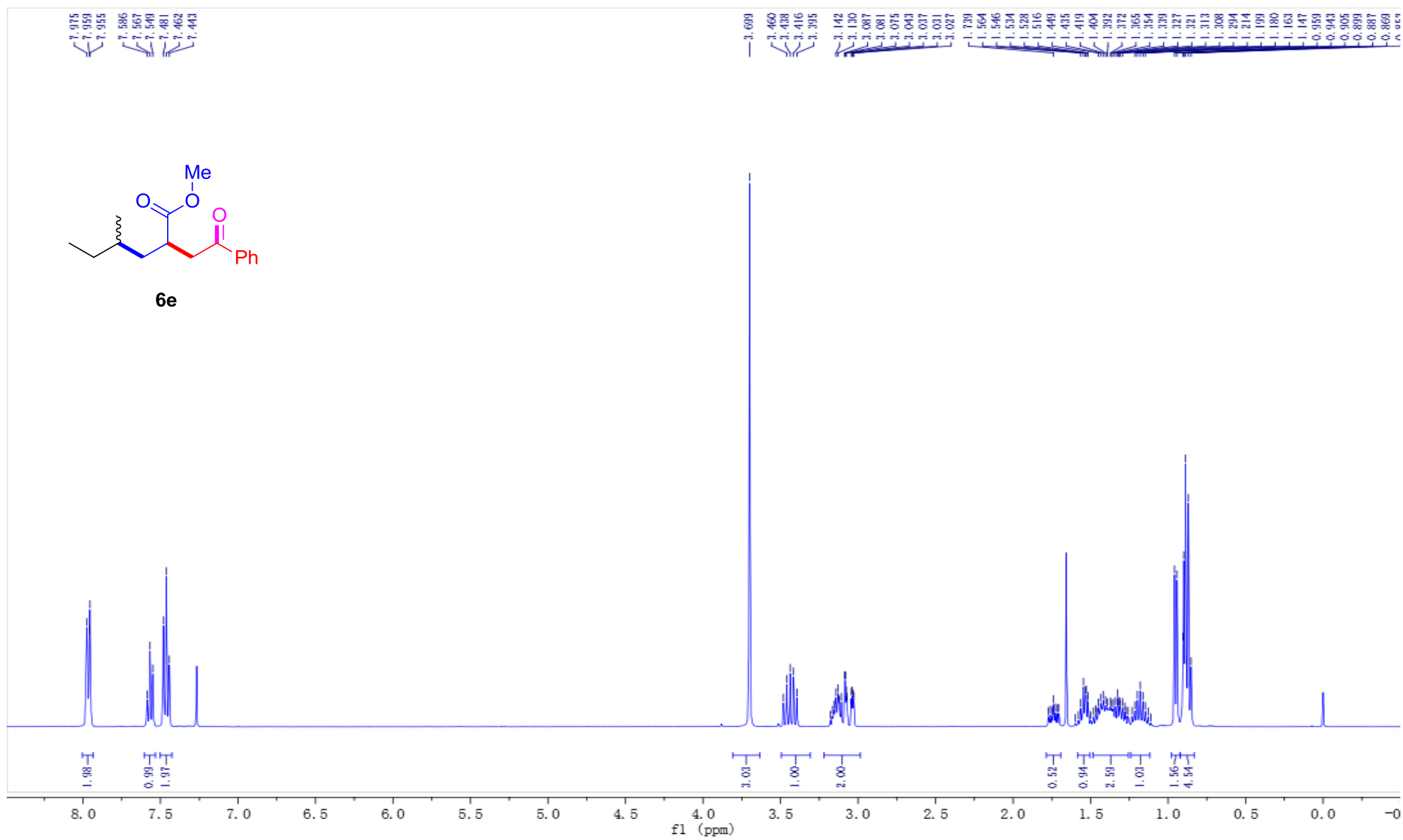


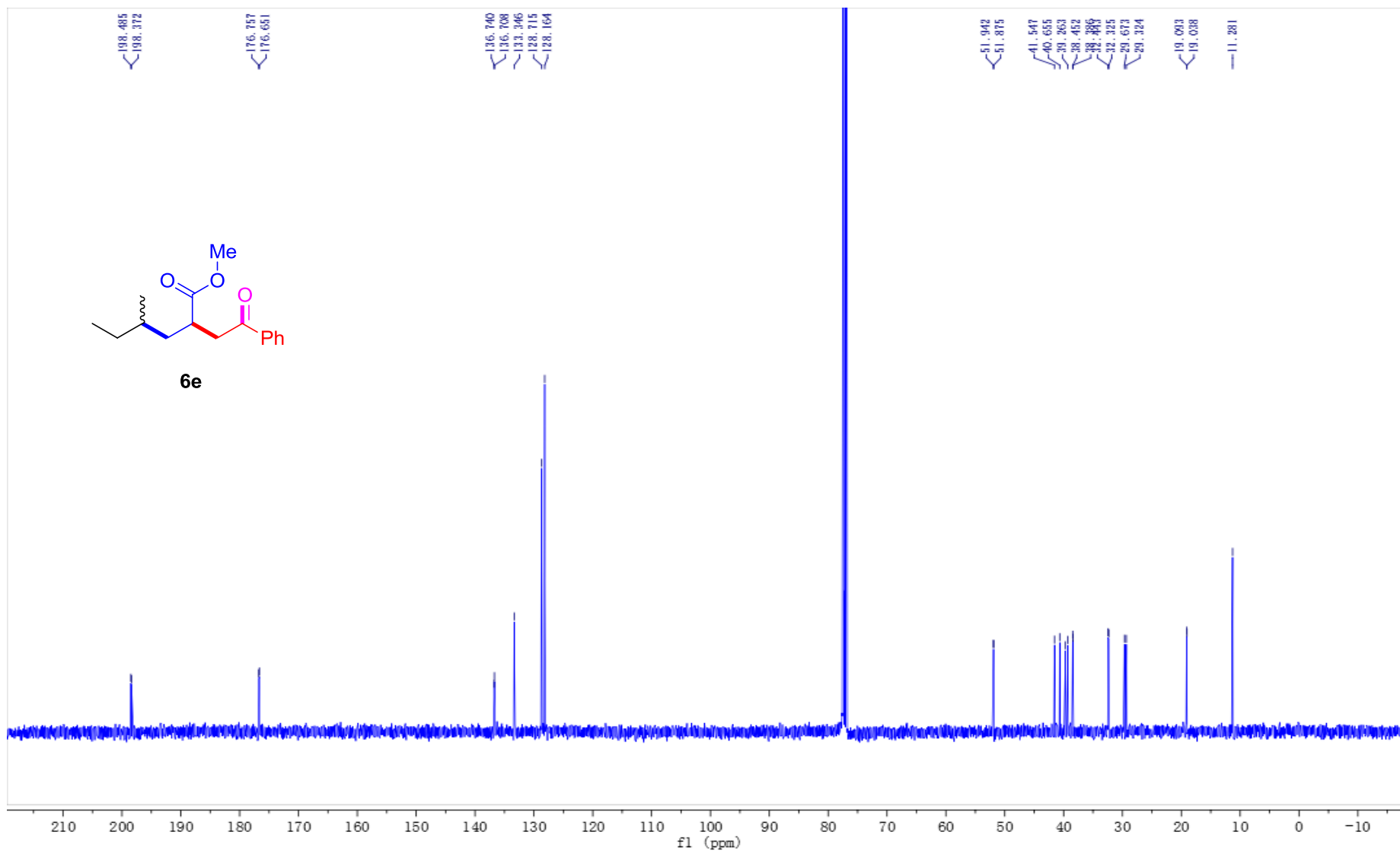


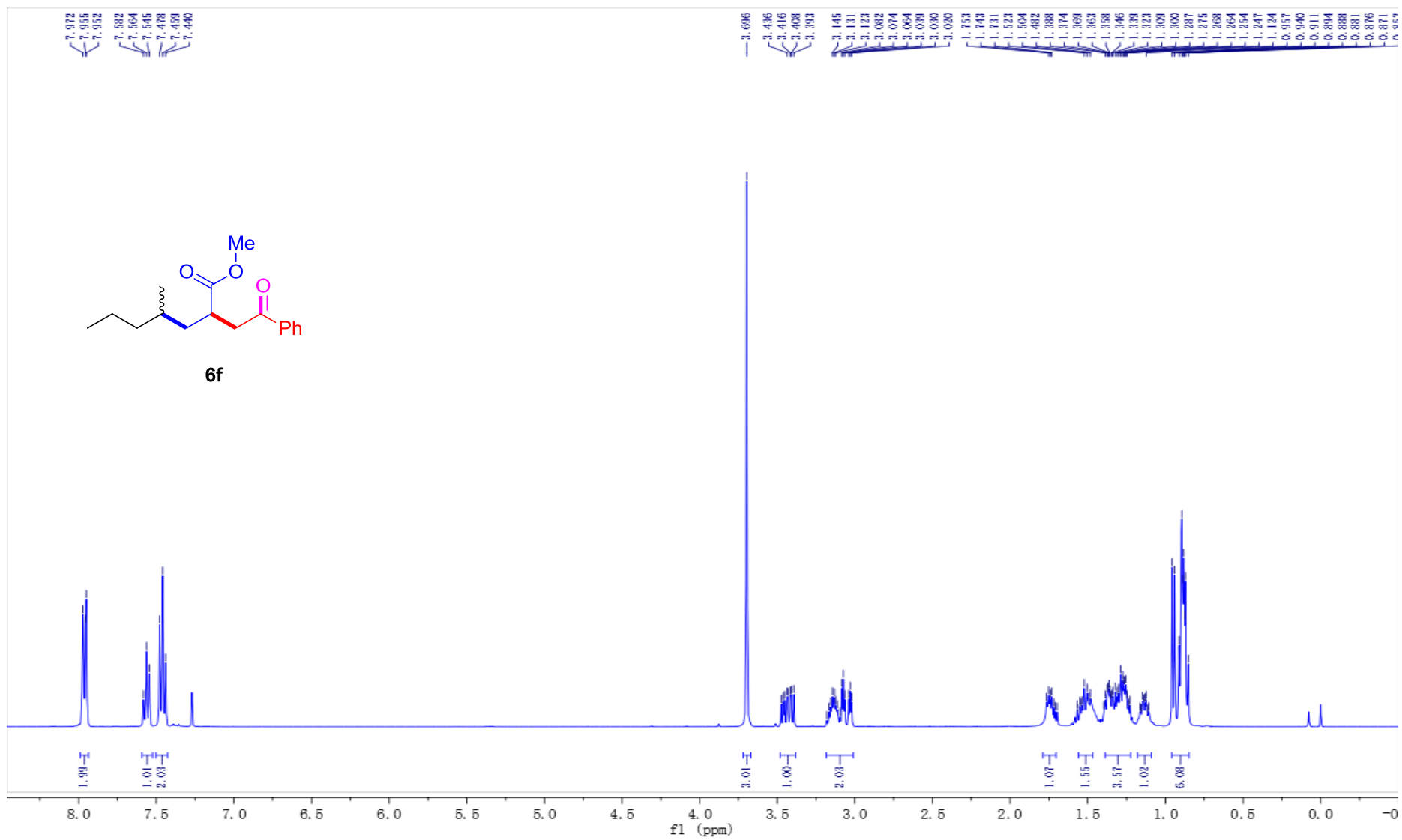


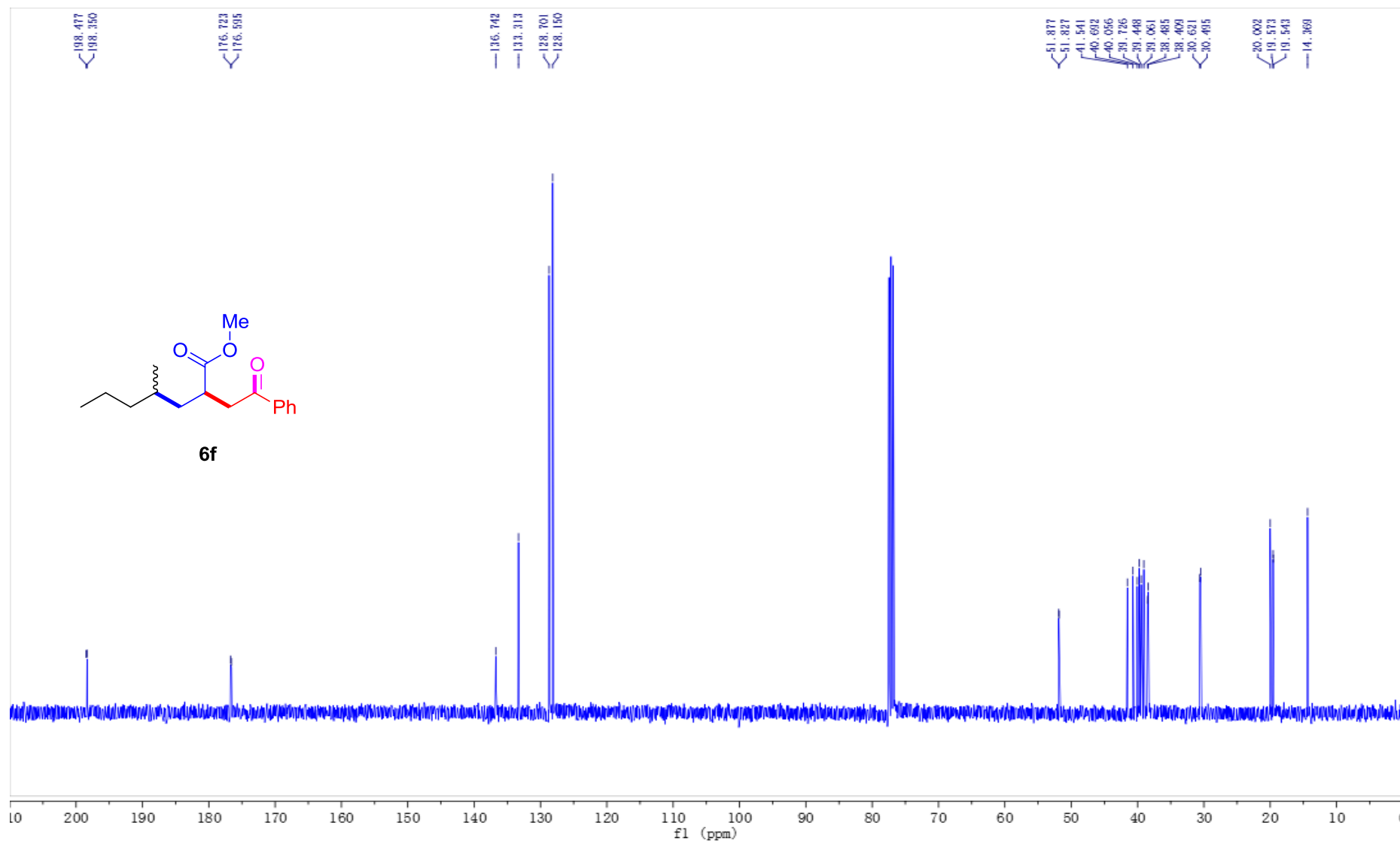


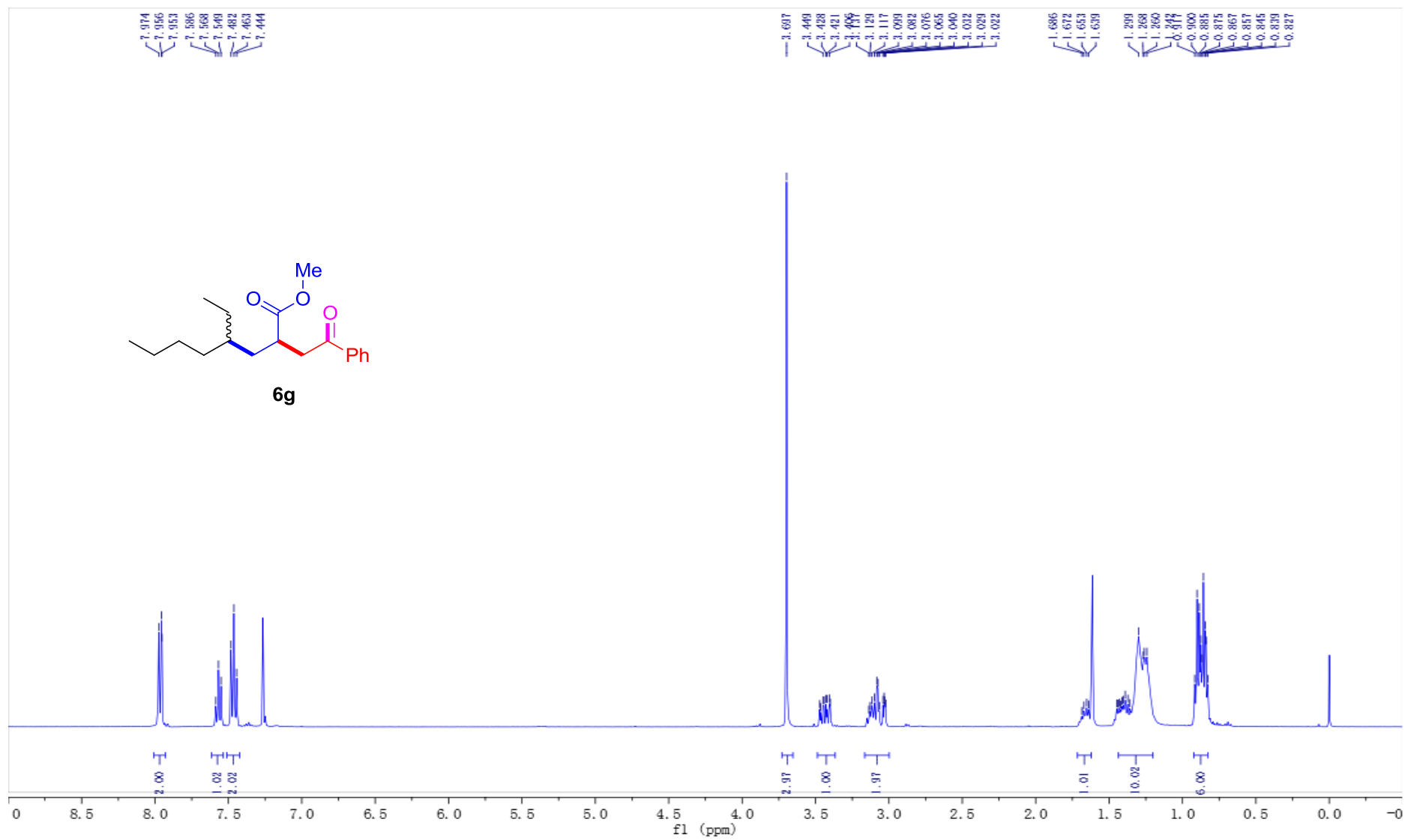




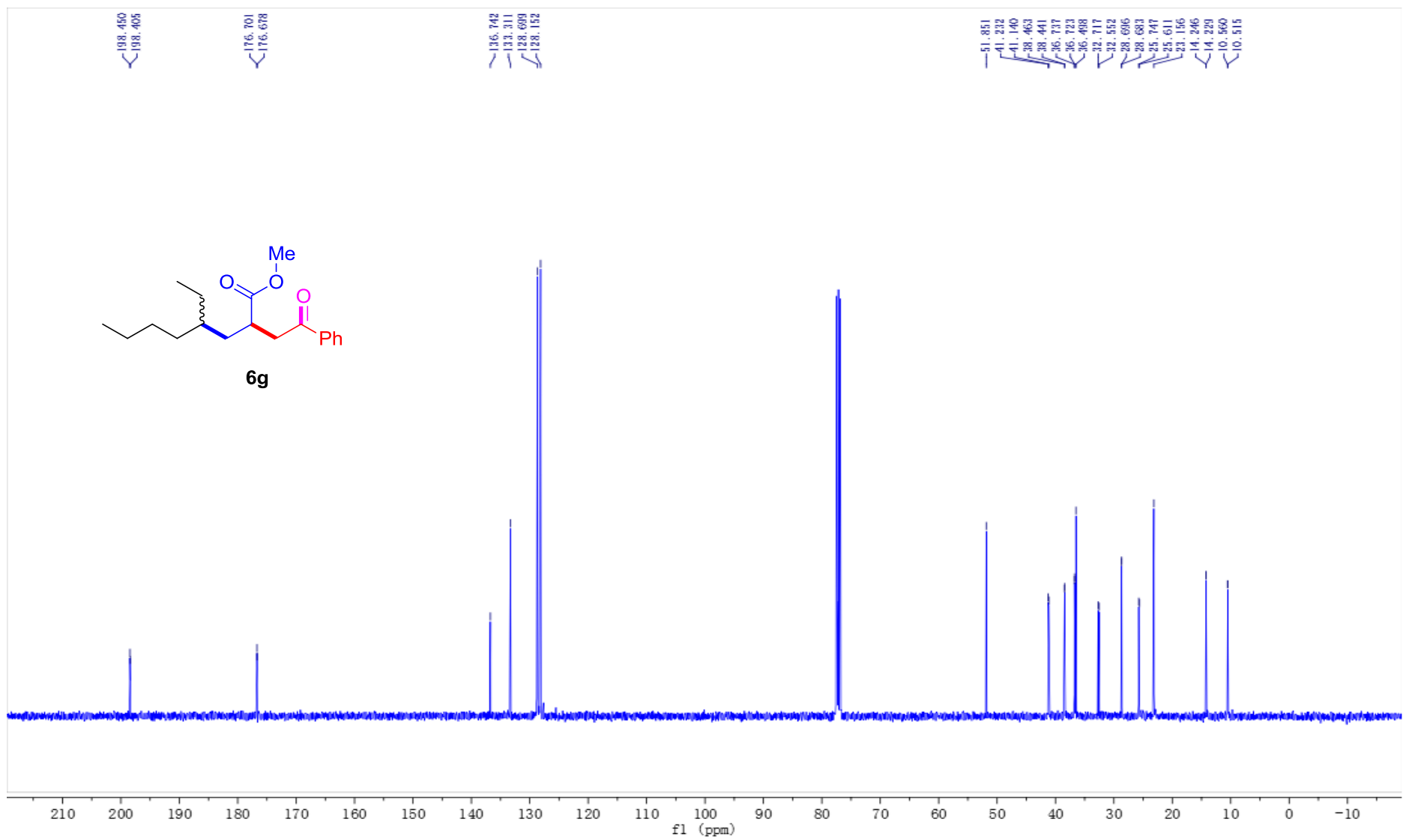


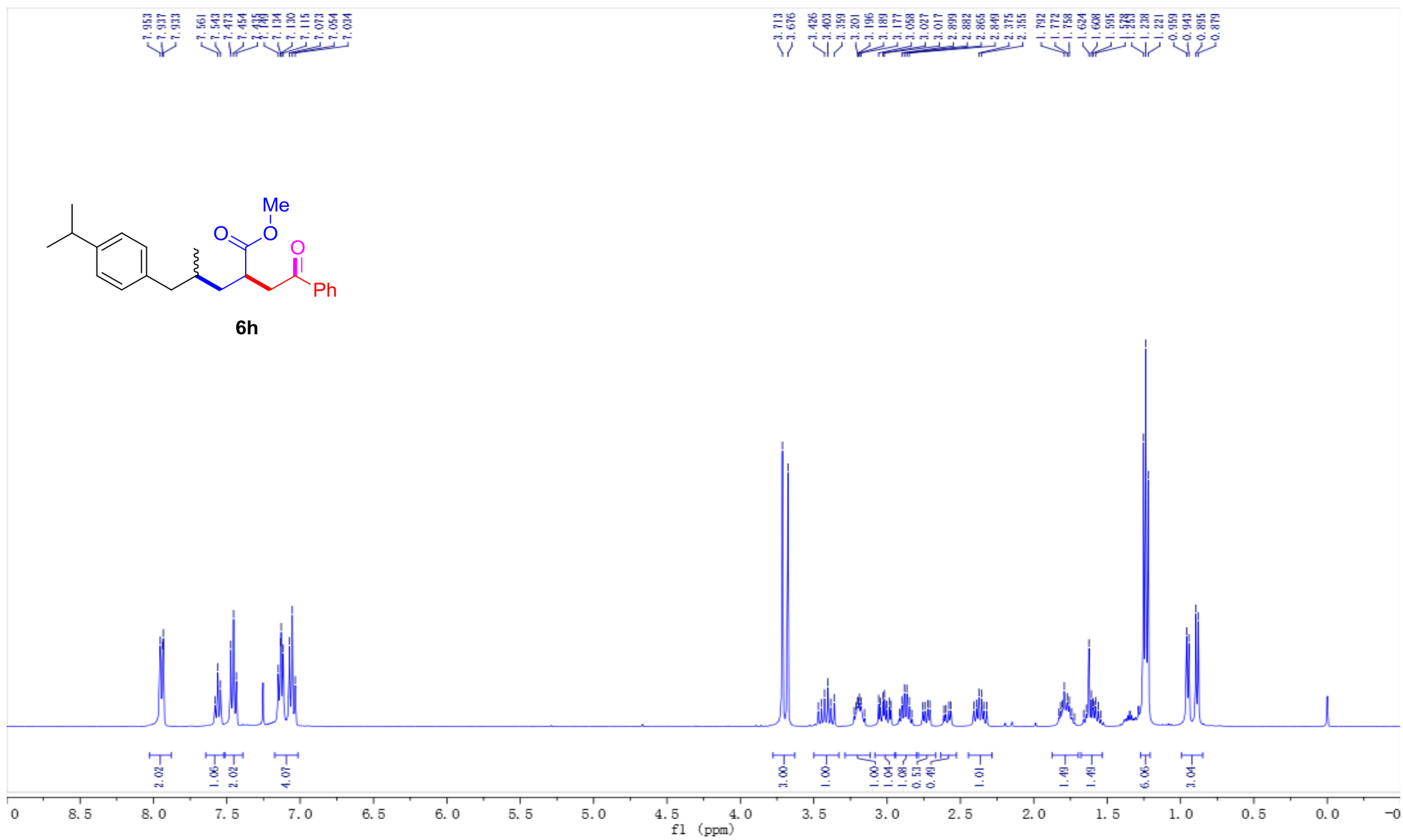


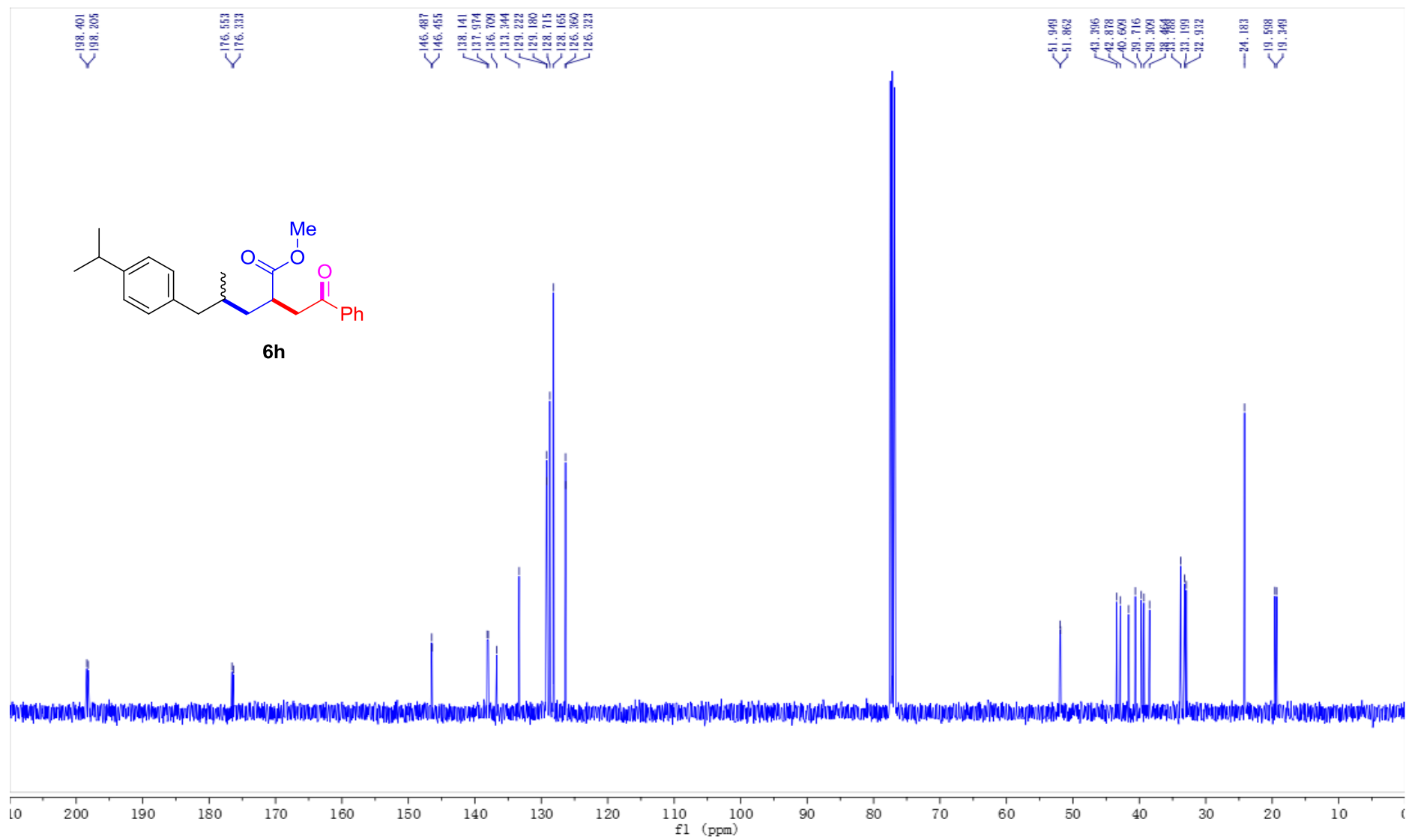


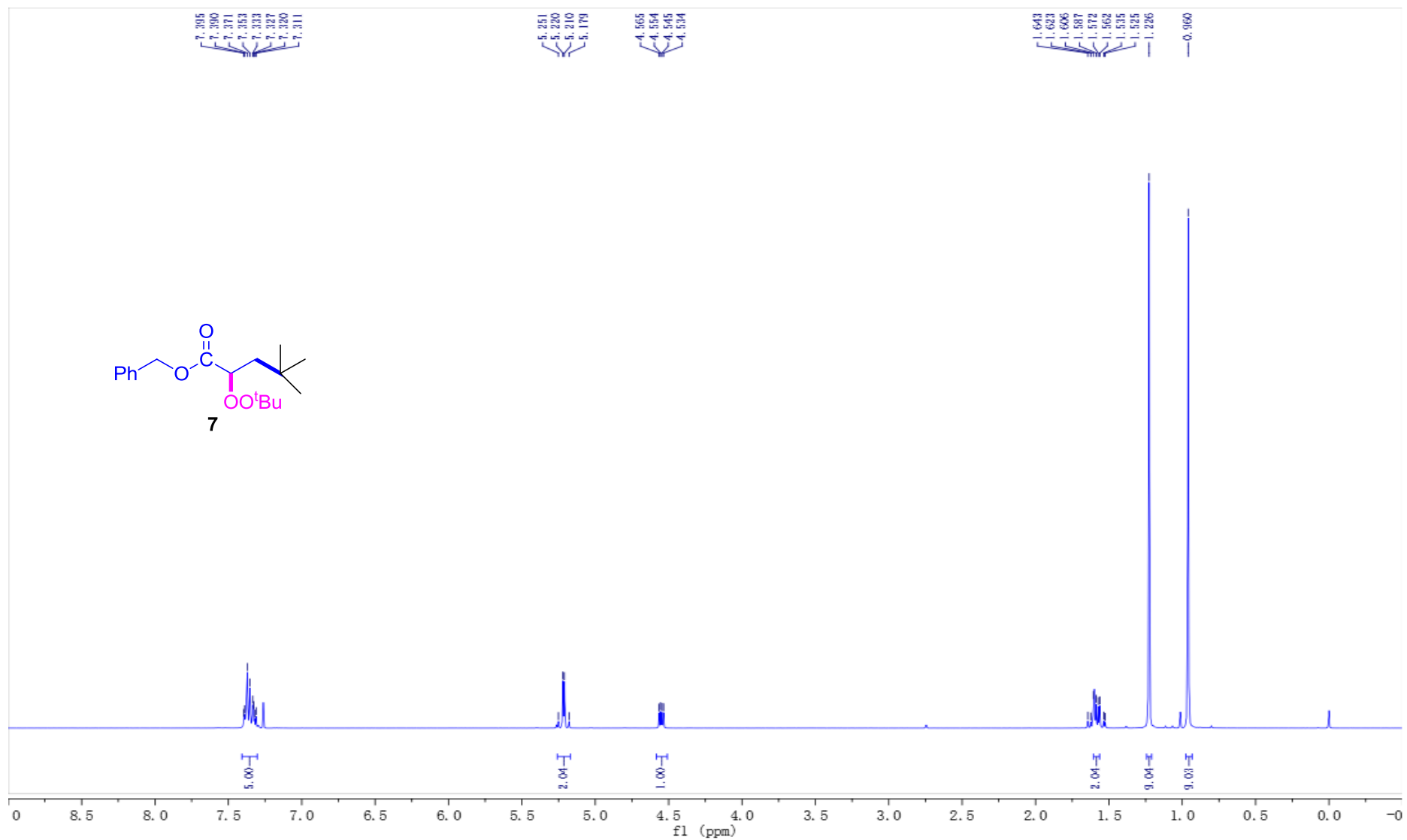


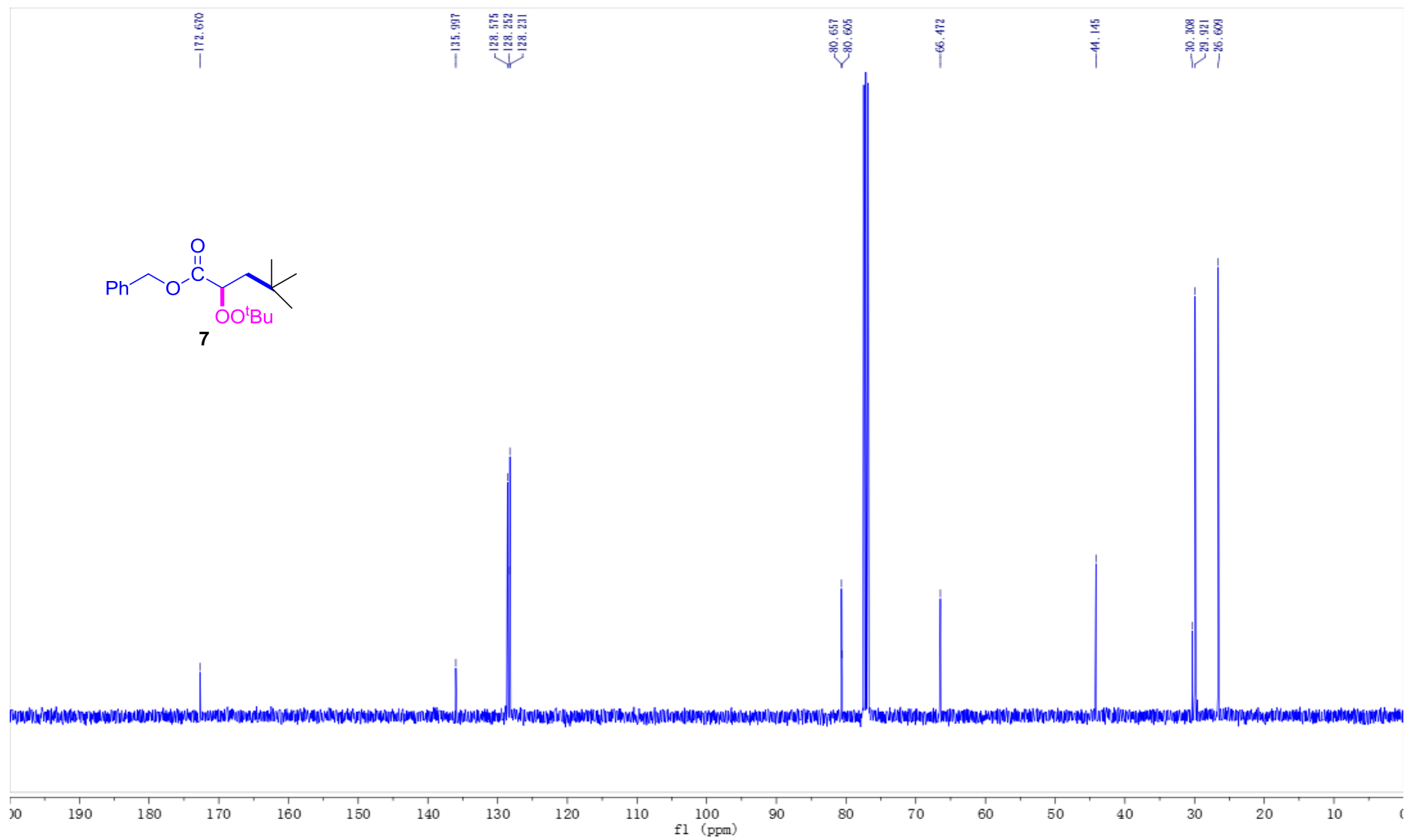


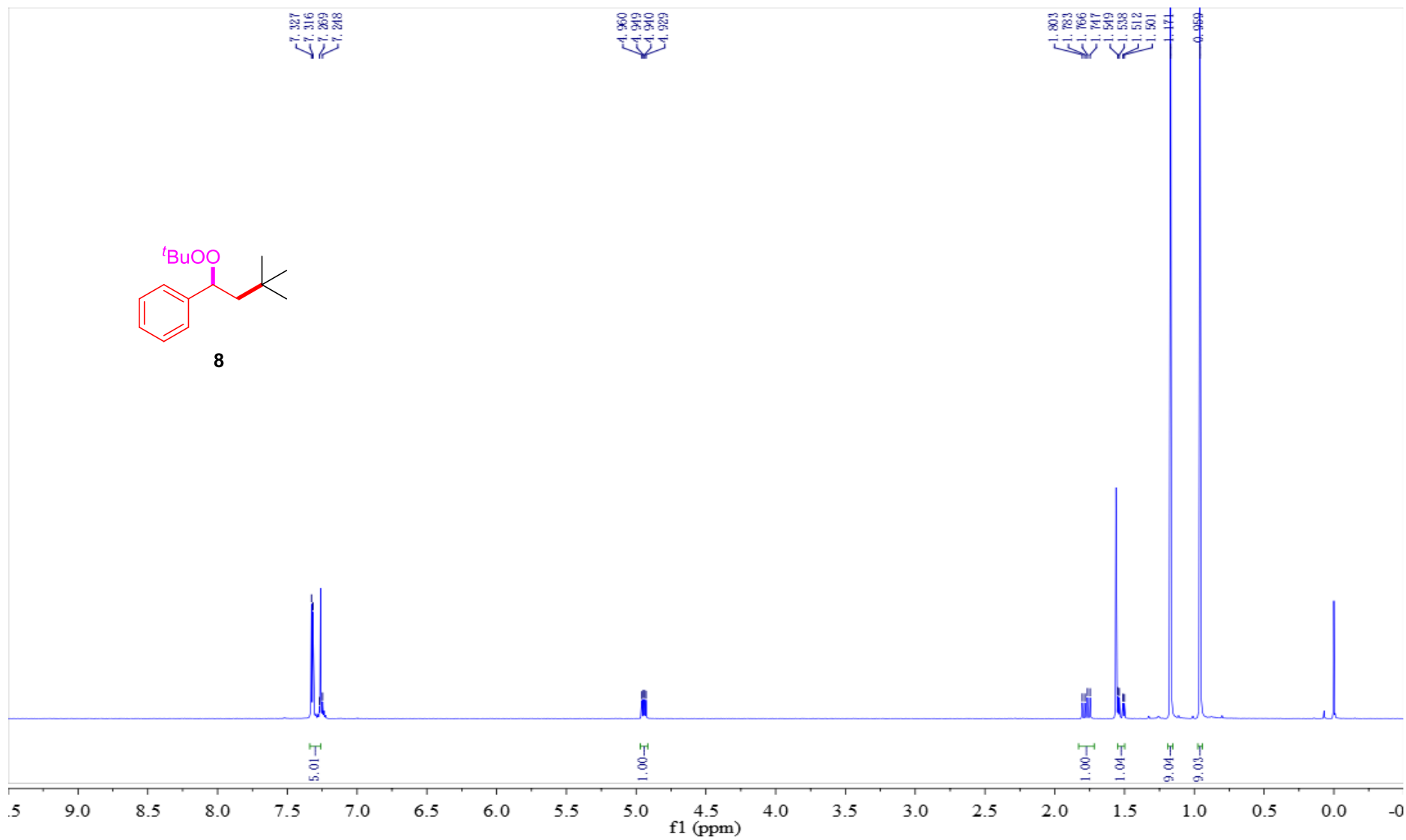


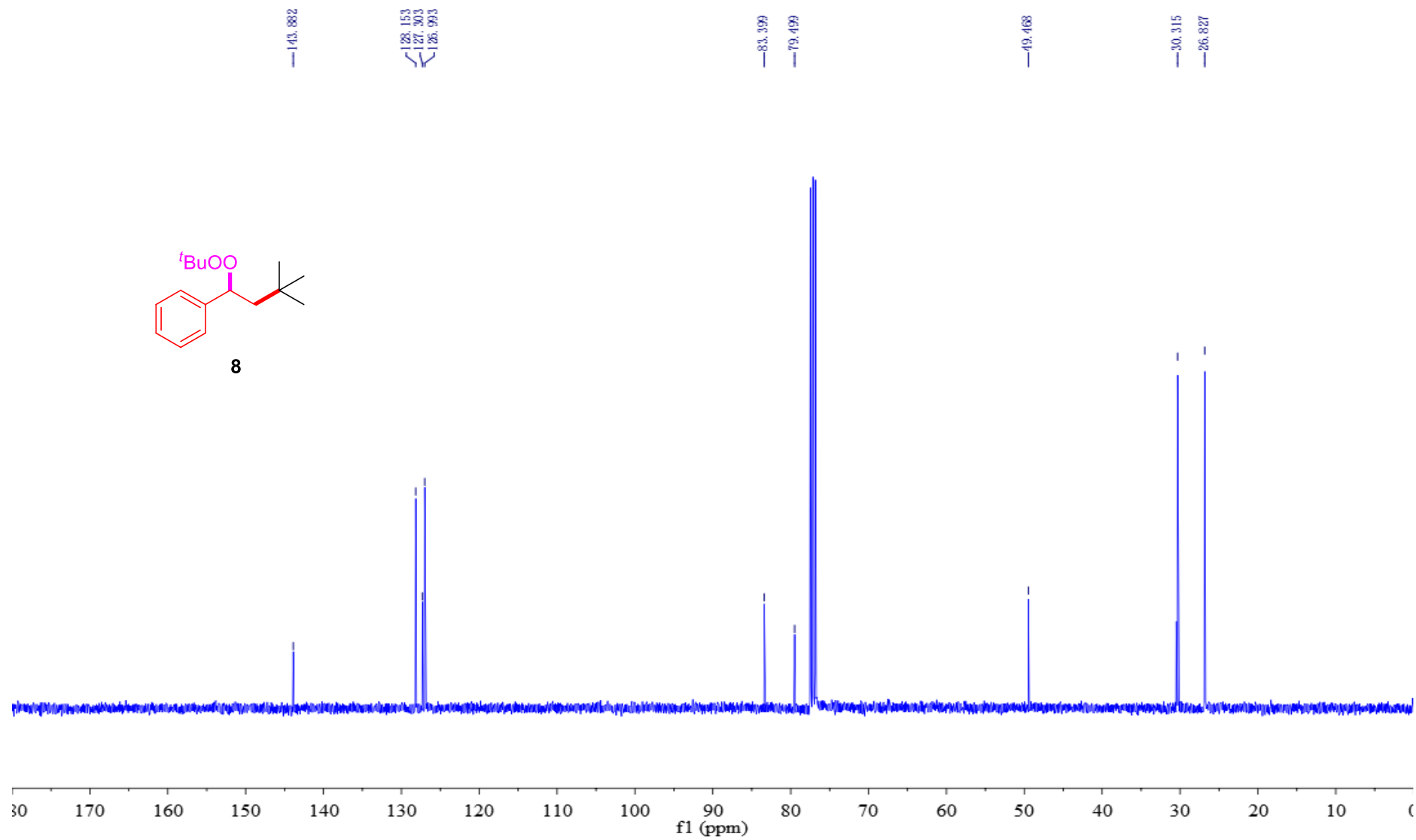
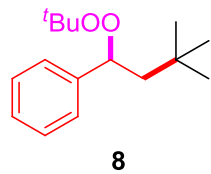


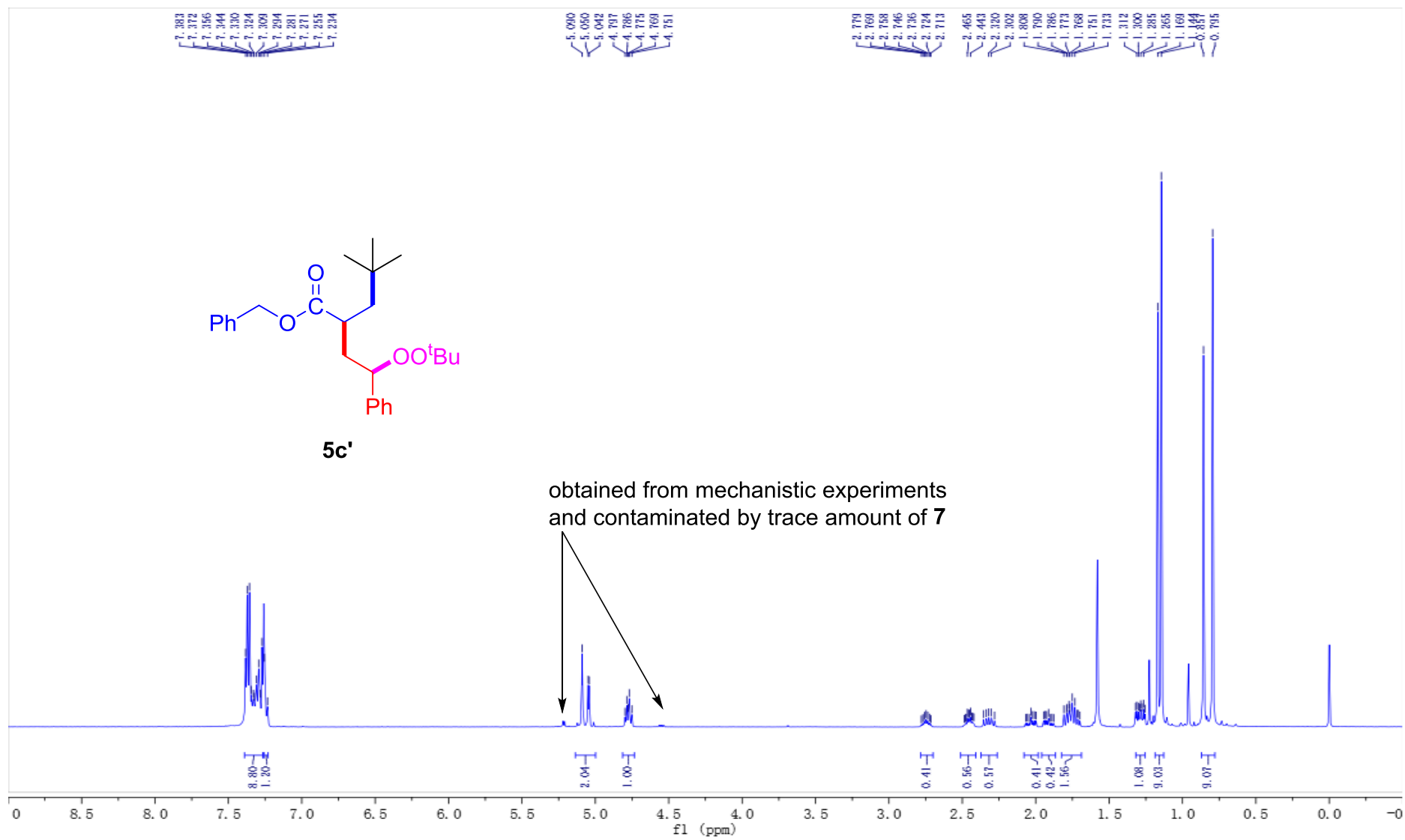






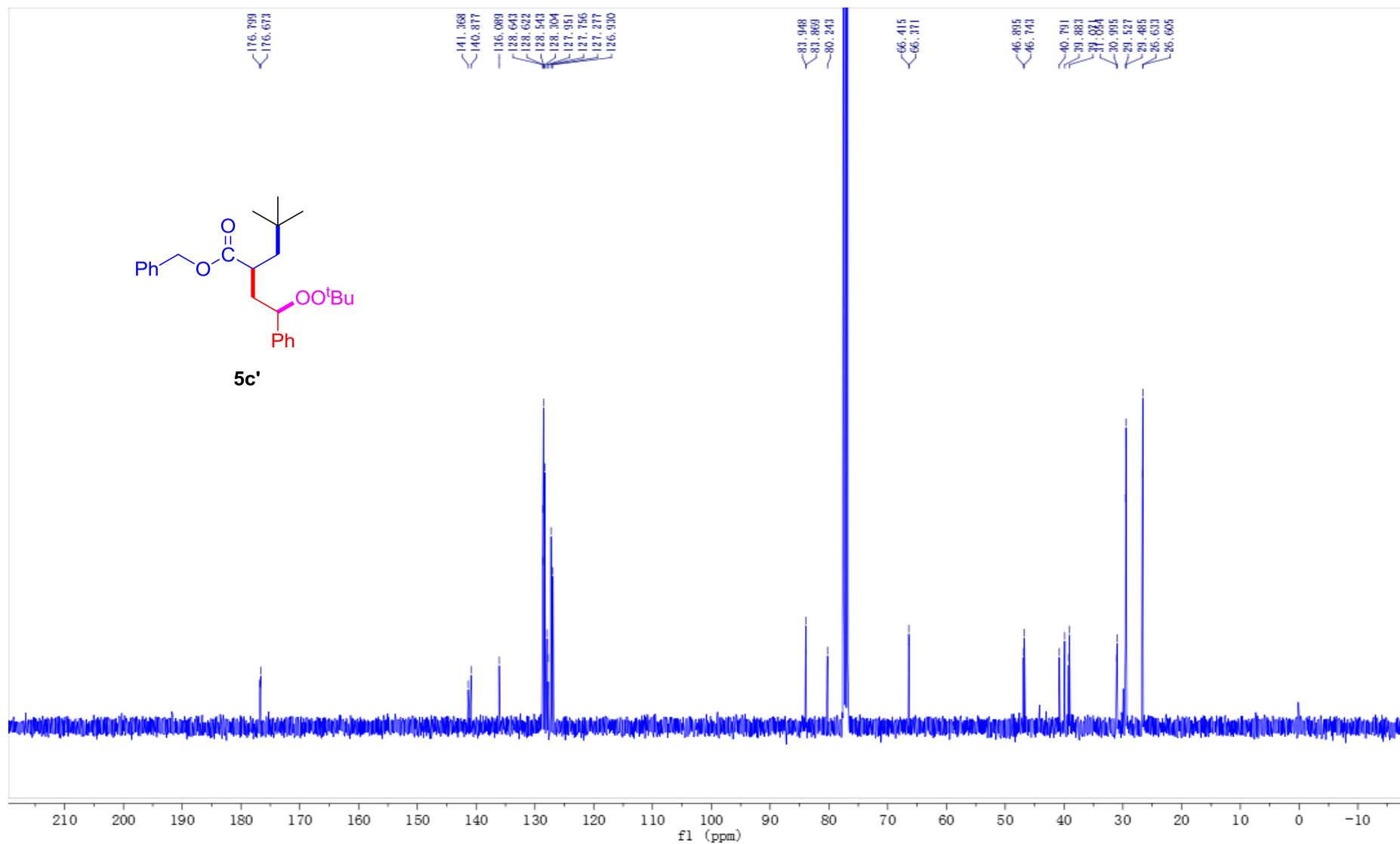


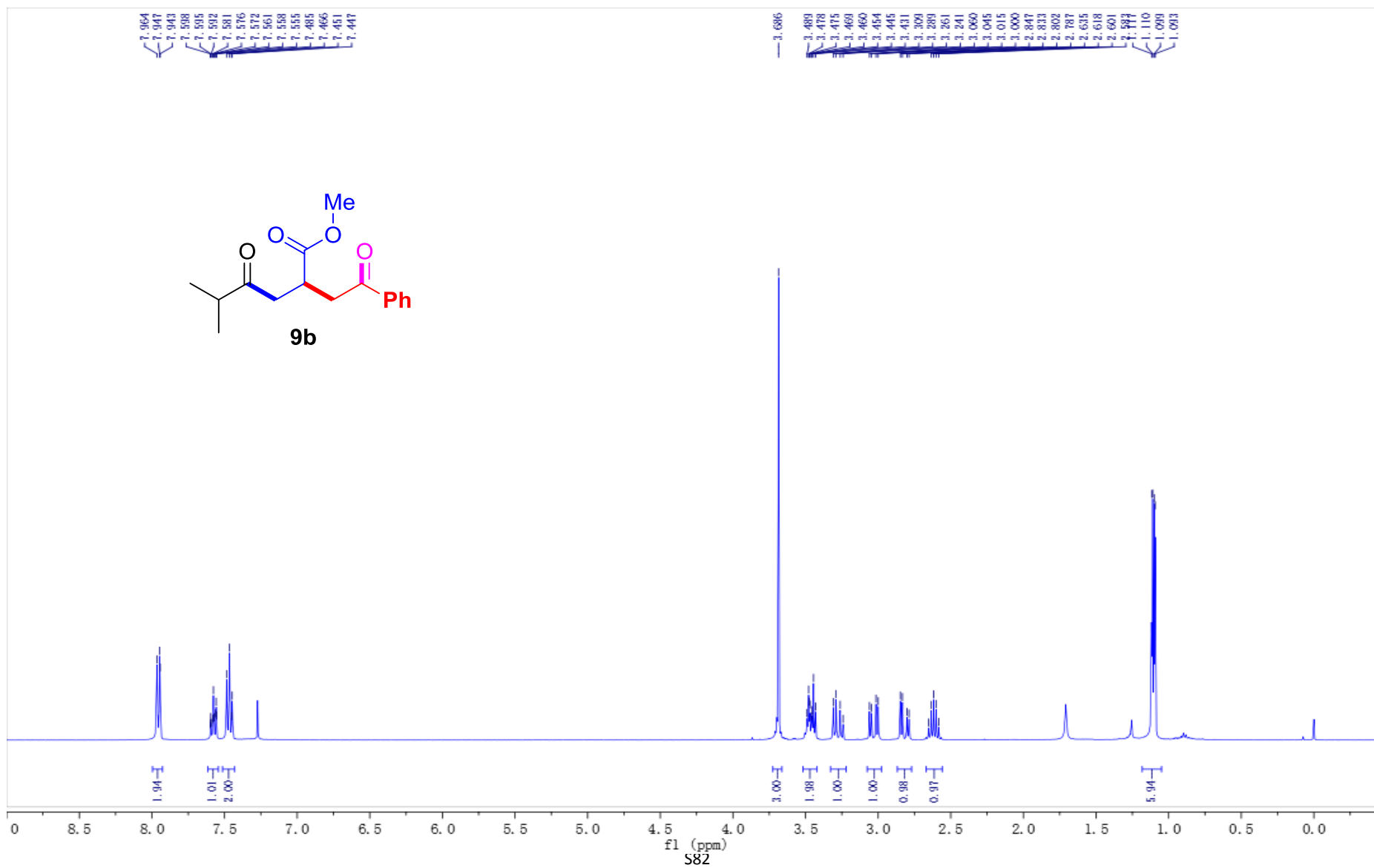


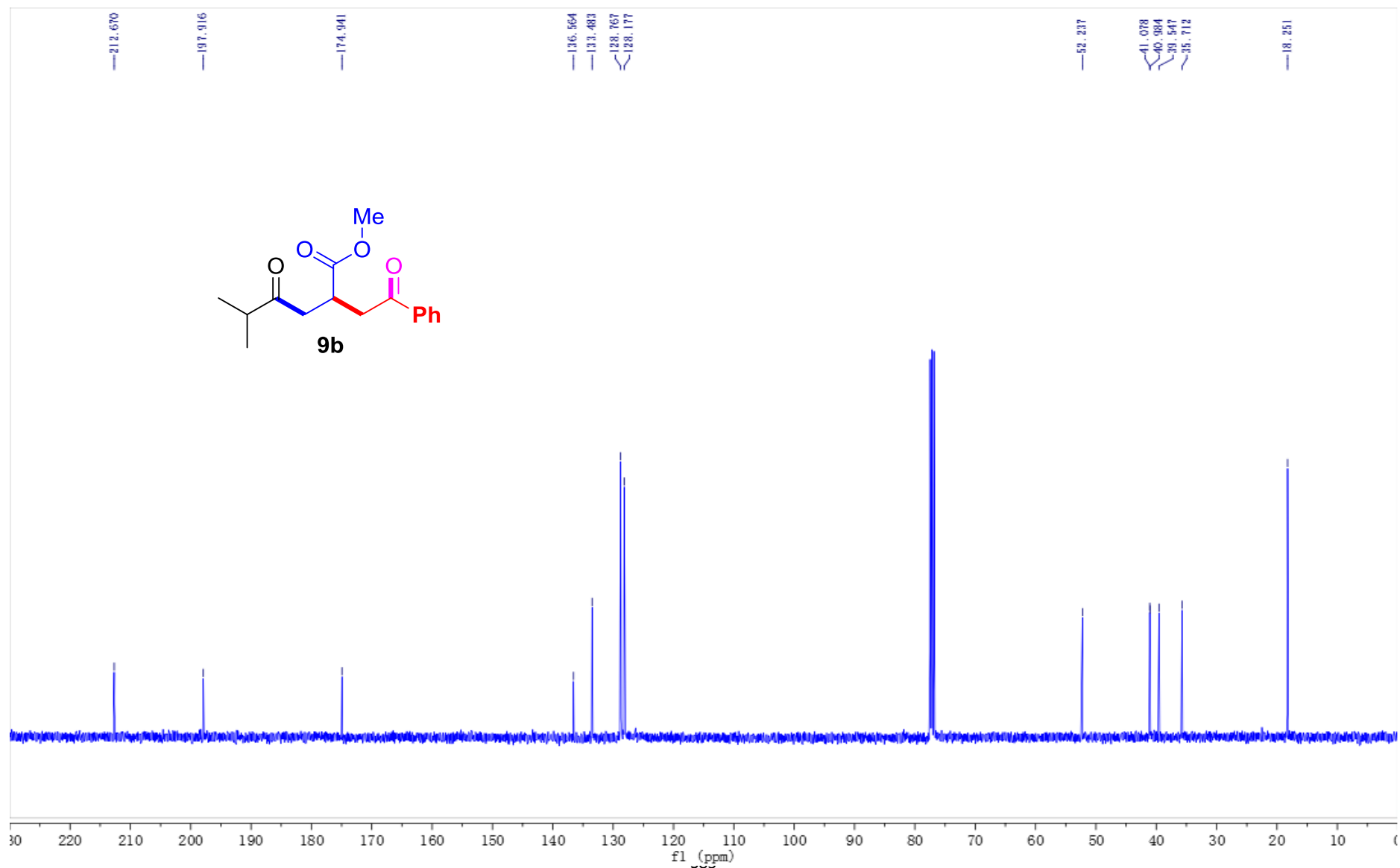


obtained from mechanistic experiments  
and contaminated by trace amount of **7**



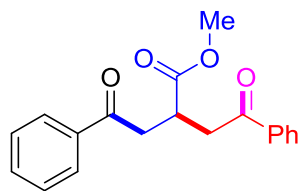






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7.964  
7.960  
7.589  
7.586  
7.571  
7.555  
7.552  
7.549  
7.481  
7.461  
7.447  
7.443

3.710  
3.698  
3.691  
3.676  
3.661  
3.647  
3.631  
3.610  
3.596  
3.565  
3.551  
3.412  
3.396  
3.367  
3.352



9i

