

## Supporting Information

### KI-Catalyzed C-S Bond Formation via Oxidation Relay Strategy: an Efficient Access to Various $\alpha$ -Thio- $\beta$ -Dicarbonyl Compounds

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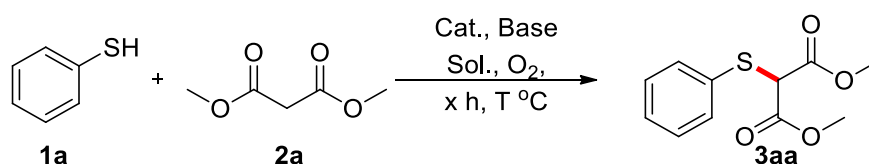
#### General Information:

All reactions were carried out in a dry solvent under argon atmosphere unless otherwise noted. NMR spectra were recorded on Bruker 400 MHz (400 MHz for <sup>1</sup>H NMR and 100 MHz for <sup>13</sup>C NMR) spectrometers. Proton chemical shifts are reported relative to a residual solvent peak (CDCl<sub>3</sub> at 7.26 ppm). Carbon chemical shifts are reported relative to a residual solvent peak (CDCl<sub>3</sub> at 77.2 ppm). The following abbreviations were used to designate multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br = broad. High-resolution mass spectra (HRMS) were measured on a Bruker Daltonics Apex II 47e Specification (for HRMS). Substrates were purchased from commercial sources and used as received. Substrates **1a-1n**, **2a-2e**, **2g**, **2j**, **2l**, **2m**, **8** are commercially available. Substrates **2f**,<sup>[1]</sup> **2h**,<sup>[2]</sup> **2i**,<sup>[2]</sup> **2k**<sup>[3]</sup> are known compounds.

### Optimization of Reaction Conditions.

A test tube equipped with a magnetic stir bar was charged with thiophenol **1a** (0.10 mmol, 1.0 eq), dimethyl malonate **2a** (0.15 mmol, 1.5 eq), catalyst (10 mol%), base (0.15 mmol, 1.5 eq) and solvent (1 mL) under oxygen atmosphere. The resulting mixture was stirred under indicated temperature for 18 h, then the reaction solution was cooled to ambient temperature. The reaction was quenched by saturated NaHCO<sub>3</sub> aqueous solution, and extracted with ethyl acetate (3\*25mL), the combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel (hexane / EtOAc = 20:1) to give **3aa** as colorless oil.

**Table S1.** Optimization of reaction conditions<sup>a</sup>.



Entry	Base	Catalyst (mol %)	Solvent	T (°C)	Yield (%)
1	K <sub>3</sub> PO <sub>4</sub>	/	DMSO	110	<10
2	K <sub>3</sub> PO <sub>4</sub>	/	DMF	110	N.R.
3	K <sub>3</sub> PO <sub>4</sub>	/	<i>n</i> -PrCN	110	27
4	K <sub>3</sub> PO <sub>4</sub>	/	CH <sub>3</sub> CN	80	28
5	K <sub>3</sub> PO <sub>4</sub>	/	CH <sub>3</sub> CN	50	13
6	DBU	/	CH <sub>3</sub> CN	80	<5
7	DMAP	/	CH <sub>3</sub> CN	80	N.R.
8	NaOH	/	CH <sub>3</sub> CN	80	46
9 <sup>b</sup>	NaOH	/	CH <sub>3</sub> CN	80	42
10 <sup>c</sup>	NaOH	/	CH <sub>3</sub> CN	80	49
11 <sup>d</sup>	NaOH	/	CH <sub>3</sub> CN	80	48
12 <sup>e</sup>	NaOH	/	CH <sub>3</sub> CN	80	62
13 <sup>e,f</sup>	NaOH	/	CH <sub>3</sub> CN	80	55
14 <sup>e</sup>	NaOH	KI (10)	CH <sub>3</sub> CN	80	89
15 <sup>e</sup>	NaOH	KBr (10)	CH <sub>3</sub> CN	80	<10
16 <sup>e</sup>	NaOH	CuI (10)	CH <sub>3</sub> CN	80	N.R.
17 <sup>e,g</sup>	NaOH	KI (10)	CH <sub>3</sub> CN	80	24
18 <sup>e,h</sup>	NaOH	KI (10)	CH <sub>3</sub> CN	80	N.R.

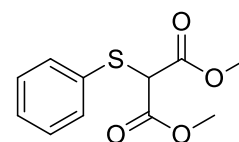
<sup>a</sup>Reaction conditions: **1a** (0.10 mmol, 1 eq), **2a** (0.15 mmol, 1.5eq), Base (0.15 mmol, 1.5 eq), Solvent (1 ml), O<sub>2</sub> (1 atm), 18h. <sup>b</sup>NaOH was used as 2.0 eq. <sup>c</sup>The reaction time was 24 h. <sup>d</sup>The reaction time was 30 h. <sup>e</sup>**2a** was used as 2.0 eq. <sup>f</sup>The mixture concentration was 0.2 mmol/mL. <sup>g</sup>Air atmosphere. <sup>h</sup>Ar atmosphere. N.R.=no result, *n*-PrCN=Butyronitrile.

### Typical procedure for thiophenol **1a** sulfuration of dimethyl malonate **2a**:

A test tube equipped with a magnetic stir bar was charged with thiophenol **1a** (0.10 mmol), dimethyl malonate **2a** (0.15 mmol), KI (10 mol%), NaOH (0.15 mmol) and CH<sub>3</sub>CN (1 mL) under O<sub>2</sub> atmosphere. The resulting mixture was stirred at 80 °C for 18 h, then quenched by saturated NaHCO<sub>3</sub> aqueous solution, and extracted with ethyl acetate (3\*25mL), the combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel (hexane / EtOAc = 20 : 1) to give **3aa** as colorless oil.

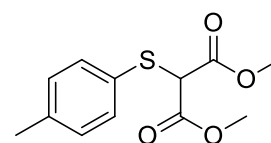
### dimethyl 2-(phenylthio)malonate (**3aa**):

21.4 mg, 89%, colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.55 – 7.50 (m, 2H), 7.35 – 7.31 (m, 3H), 4.55 (s, 1H), 3.76 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 167.0, 133.6, 132.2, 129.4, 129.0, 55.5, 53.5; IR (KBr, ν / cm<sup>-1</sup>) 3423, 2976 1740, 1258, 1150, 723, 669; HRMS (ESI<sup>+</sup>) Calcd for C<sub>11</sub>H<sub>12</sub>O<sub>4</sub>S (M+Na<sup>+</sup>) 263.0349, Found 263.0351.



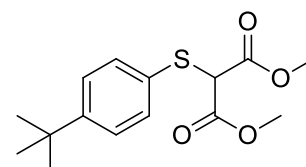
### dimethyl 2-(p-tolylthio)malonate (**3ba**):

21.8 mg, 86%, colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 4.50 (s, 1H), 3.75 (s, 6H), 2.34 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 167.1, 139.5, 134.2, 130.2, 128.4, 55.8, 53.4, 21.4; IR (KBr, ν / cm<sup>-1</sup>) 2956, 1739, 1295, 1262, 1146, 1019, 813; HRMS (ESI<sup>+</sup>) Calcd for C<sub>12</sub>H<sub>14</sub>O<sub>4</sub>S (M+Na<sup>+</sup>) 277.0505, Found 277.0497.



### dimethyl 2-((4-(tert-butyl)phenyl)thio)malonate (**3ca**):

25.8 mg, 87%, colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.46 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 4.50 (s, 1H), 3.75 (s, 6H), 1.30 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 167.1, 152.5, 133.7, 128.6, 126.5, 55.7, 53.4, 34.9, 31.4; IR (KBr, ν / cm<sup>-1</sup>) 2961, 1761, 1269, 1491, 1437, 1150, 1016, 835; HRMS (ESI<sup>+</sup>) Calcd for C<sub>15</sub>H<sub>20</sub>O<sub>4</sub>S (M+Na<sup>+</sup>)



319.0975, Found 319.0976.

**dimethyl 2-((4-methoxyphenyl)thio)malonate (3da):**

24.6 mg, 91%, colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ

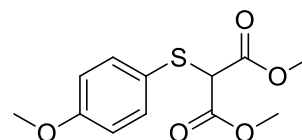
7.50 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 4.41 (s,

1H), 3.80 (s, 3H), 3.74 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

δ 167.1, 160.9, 136.9, 122.1, 114.9, 56.2, 55.5, 53.3; IR (KBr, ν / cm<sup>-1</sup>) 2956, 2817,

1580, 1213, 729; HRMS (ESI<sup>+</sup>) Calcd for C<sub>12</sub>H<sub>14</sub>O<sub>5</sub>S (M+Na<sup>+</sup>) 293.0454, Found

293.0451.



**dimethyl 2-((4-fluorophenyl)thio)malonate (3ea):**

23.2 mg, 90%, colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ

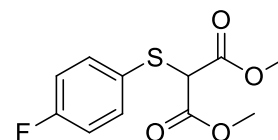
7.47 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 4.50 (s, 1H),

3.76 (s, 7H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 166.9, 164.9,

162.4, 136.9, 136.8, 126.9, 116.7, 116.4, 55.8, 53.5; IR (KBr, ν / cm<sup>-1</sup>) 2961, 2920, 1737,

1491, 1262, 1025, 800, 669; HRMS (ESI<sup>+</sup>) Calcd for C<sub>11</sub>H<sub>11</sub>FO<sub>4</sub>S (M+Na<sup>+</sup>) 281.0254,

Found 281.0260.



**dimethyl 2-((4-chlorophenyl)thio)malonate (3fa):**

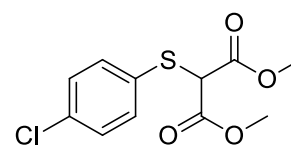
23.8 mg, 87%, colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ

7.47 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 4.50 (s, 1H),

3.76 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 166.8, 135.5,

135.2, 130.5, 129.6, 55.4, 53.5; IR (KBr, ν / cm<sup>-1</sup>) 2956, 1739, 1478, 1437, 1264, 1150,

1096, 822; HRMS (ESI<sup>+</sup>) Calcd for C<sub>11</sub>H<sub>11</sub>ClO<sub>4</sub>S (M+Na<sup>+</sup>) 296.9959, Found 296.9960.



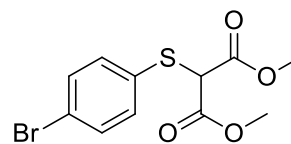
**dimethyl 2-((4-bromophenyl)thio)malonate (3ga):**

27.0 mg, 85%, colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ

7.46 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 4.50 (s, 1H),

3.76 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 166.8, 135.2,

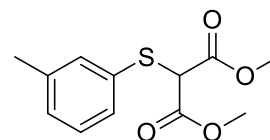
132.5, 131.2, 123.6, 55.2, 53.6; IR (KBr, ν / cm<sup>-1</sup>) 2958, 1759, 1478, 1437, 1305, 1262,



1165, 807; HRMS (ESI<sup>+</sup>) Calcd for C<sub>11</sub>H<sub>11</sub>BrO<sub>4</sub>S (M+Na<sup>+</sup>) 340.9454, Found 340.9449.

**dimethyl 2-(m-tolylthio)malonate (3ha):**

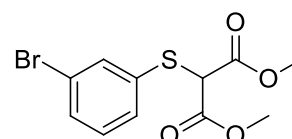
20.6 mg, 81%, colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.33 (d, *J* = 12.5 Hz, 2H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 7.4 Hz, 1H), 4.54 (s, 1H), 3.76 (s, 6H), 2.33 (s, 3H); <sup>13</sup>C NMR (100



MHz, CDCl<sub>3</sub>) δ 167.1, 139.3, 134.0, 132.0, 130.4, 129.8, 129.2, 55.6, 53.5, 21.4; IR (KBr, ν / cm<sup>-1</sup>) 2956, 1739, 1437, 1265, 1150, 1023, 783, 693; HRMS (ESI<sup>+</sup>) Calcd for C<sub>12</sub>H<sub>14</sub>O<sub>4</sub>S (M+Na<sup>+</sup>) 277.0505, Found 277.0505.

**dimethyl 2-((3-bromophenyl)thio)malonate (3ia):**

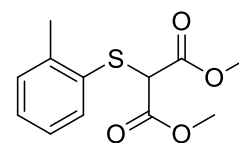
27.0 mg, 85%, colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.68 (t, *J* = 1.6 Hz, 1H), 7.46 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.20 (t, *J* = 7.9 Hz, 1H), 4.54 (s, 1H), 3.77 (s, 7H); <sup>13</sup>C NMR (100



MHz, CDCl<sub>3</sub>) δ 166.7, 135.8, 134.4, 132.0, 131.8, 130.7, 122.9, 55.2, 53.6; IR (KBr, ν / cm<sup>-1</sup>) 2958, 1757, 1432, 1314, 1262, 1170, 799; HRMS (ESI<sup>+</sup>) Calcd for C<sub>11</sub>H<sub>11</sub>BrO<sub>4</sub>S (M+Na<sup>+</sup>) 340.9454, Found 340.9456.

**dimethyl 2-(o-tolylthio)malonate (3ja):**

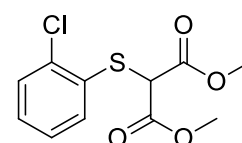
18.3 mg, 72%, colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.49 (d, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 4.0 Hz, 2H), 7.19 – 7.14 (m, 1H), 4.49 (s, 1H), 3.75 (s, 6H), 2.48 (s, 3H); <sup>13</sup>C NMR (100 MHz,



CDCl<sub>3</sub>) δ 166.8, 141.1, 134.1, 131.3, 130.7, 129.0, 126.8, 54.6, 53.3, 20.7; IR (KBr, ν / cm<sup>-1</sup>) 2952, 1740, 1436, 1228, 1151, 1029, 763, 689; HRMS (ESI<sup>+</sup>) Calcd for C<sub>12</sub>H<sub>14</sub>O<sub>4</sub>S (M+Na<sup>+</sup>) 277.0505, Found 277.0502.

**dimethyl 2-((2-chlorophenyl)thio)malonate (3ka):**

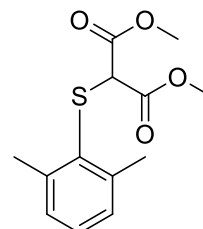
20.3 mg, 74%, colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.58 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.44 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.28 (d, *J* = 1.7 Hz, 1H), 7.24 (d, *J* = 1.4 Hz, 1H), 4.70 (s, 1H), 3.76 (s, 6H); <sup>13</sup>C NMR (100 MHz,



CDCl<sub>3</sub>)  $\delta$  166.6, 137.7, 135.0, 131.2, 130.4, 130.2, 127.6, 53.7, 53.6; IR (KBr,  $\nu$  / cm<sup>-1</sup>) 2958, 1750 1468, 1263, 1158, 1121, 819; HRMS (ESI<sup>+</sup>) Calcd for C<sub>11</sub>H<sub>11</sub>ClO<sub>4</sub>S (M+Na<sup>+</sup>) 296.9959, Found 296.9960.

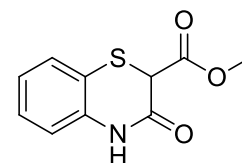
**dimethyl 2-((2,6-dimethylphenyl)thio)malonate (3la):**

16.9 mg, 63%, colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.18 – 7.14 (m, 1H), 7.11 (d, *J* = 6.7 Hz, 2H), 4.27 (s, 1H), 3.72 (s, 6H), 2.53 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  167.2, 144.0, 130.4, 129.8, 128.6, 54.1, 53.3, 21.9; IR (KBr,  $\nu$  / cm<sup>-1</sup>) 2958, 1741, 1437, 1271, 1153, 1016, 779; HRMS (ESI<sup>+</sup>) Calcd for C<sub>13</sub>H<sub>16</sub>O<sub>4</sub>S (M+Na<sup>+</sup>) 291.0662, Found 291.0660.



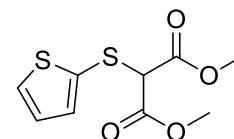
**methyl 3,4-dihydro-2H-benzo[b][1,4]thiazine-2-carboxylate (3ma):**

17.7 mg, 76%, white powder; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.78 (s, 1H), 7.33 (d, *J* = 7.5 Hz, 1H), 7.22 (dd, *J* = 11.0, 4.4 Hz, 1H), 7.05 (td, *J* = 7.7, 1.1 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 4.26 (s, 1H), 3.72 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  167.4, 163.0, 135.9, 128.1, 128.0, 124.5, 124.1, 117.5, 117.0, 53.6, 45.1; IR (KBr,  $\nu$  / cm<sup>-1</sup>) 3058, 2920, 1739, 1681, 1482, 1265, 740; HRMS (ESI<sup>+</sup>) Calcd for C<sub>10</sub>H<sub>9</sub>NO<sub>3</sub>S (M+Na<sup>+</sup>) 246.0195, Found 246.0199.



**dimethyl 2-(thiophen-2-ylthio)malonate (3na):**

20.7 mg, 84%, colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.46 (d, *J* = 5.3 Hz, 1H), 7.29 (d, *J* = 3.4 Hz, 1H), 7.05 – 6.98 (m, 1H), 4.43 (s, 1H), 3.77 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  166.5, 137.5, 132.4, 129.1, 127.9, 57.4, 53.5; IR (KBr,  $\nu$  / cm<sup>-1</sup>) 2954, 1737, 1435, 1262, 1150, 708; HRMS (ESI<sup>+</sup>) Calcd for C<sub>9</sub>H<sub>10</sub>O<sub>4</sub>S<sub>2</sub> (M+Na<sup>+</sup>) 268.9913, Found 268.9914.

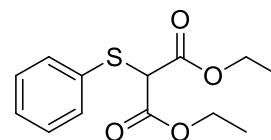


**diethyl 2-(phenylthio)malonate (3ab):**

22.0 mg, 82%, colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54

(dd,  $J = 6.5, 2.9$  Hz, 2H), 7.39 – 7.29 (m, 3H), 4.53 (s, 1H), 4.21

(q,  $J = 7.1$  Hz, 4H), 1.23 (t,  $J = 7.1$  Hz, 6H);  $^{13}\text{C}$  NMR (100



MHz,  $\text{CDCl}_3$ )  $\delta$  166.6, 133.5, 132.5, 129.3, 128.8, 62.6, 55.8, 14.1; IR (KBr,  $\nu / \text{cm}^{-1}$ )

3457, 2984, 1735, 1301, 1150, 1027, 751, 691; HRMS ( $\text{ESI}^+$ ) Calcd for  $\text{C}_{13}\text{H}_{16}\text{O}_4\text{S}$

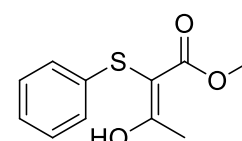
( $\text{M}+\text{Na}^+$ ) 291.0662, Found 291.0662.

**(Z)-methyl 3-hydroxy-2-(phenylthio)but-2-enoate (3ac):**

19.3 mg, 86%, colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  13.80

(s, 1H), 7.25 (t,  $J = 7.7$  Hz, 2H), 7.12 (t,  $J = 6.5$  Hz, 3H), 3.77 (d,

$J = 11.0$  Hz, 4H), 2.34 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$



185.4, 173.6, 138.1, 132.7, 129.1, 125.4, 125.3, 91.8, 52.9, 21.1; IR (KBr,  $\nu / \text{cm}^{-1}$ )

3448, 2954, 1741, 1441, 1258, 744, 691; HRMS ( $\text{ESI}^+$ ) Calcd for  $\text{C}_{11}\text{H}_{12}\text{O}_3\text{S}$  ( $\text{M}+\text{Na}^+$ )

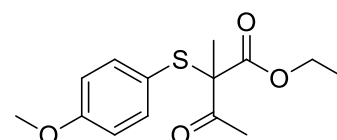
247.0399, Found 247.0343.

**ethyl 2-((4-methoxyphenyl)thio)-2-methyl-3-oxobutanoate (3ad):**

21.4 mg, 76%, colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

$\delta$  7.34 (d,  $J = 8.7$  Hz, 2H), 6.84 (d,  $J = 8.7$  Hz, 2H), 4.25

(q,  $J = 7.1$  Hz, 2H), 3.81 (d,  $J = 6.4$  Hz, 3H), 2.36 (s, 3H),



1.47 (s, 3H), 1.29 (t,  $J = 7.1$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  199.5, 170.2,

161.3, 138.9, 120.0, 114.7, 65.9, 62.5, 55.5, 26.2, 20.7, 14.2; IR (KBr,  $\nu / \text{cm}^{-1}$ ) 2984,

2939, 1716, 1593, 1495, 1251, 1098, 1029, 833; HRMS ( $\text{ESI}^+$ ) Calcd for  $\text{C}_{14}\text{H}_{18}\text{O}_4\text{S}$

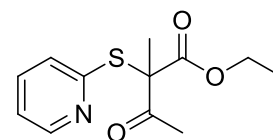
( $\text{M}+\text{Na}^+$ ) 305.0818, Found 305.0819.

**ethyl 2-methyl-3-oxo-2-(pyridin-2-ylthio)butanoate (3ae):**

17.5 mg, 69%, colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.36

(s, 1H), 7.53 (t,  $J = 7.4$  Hz, 1H), 7.24 (s, 1H), 7.09 – 7.00 (m,

1H), 4.23 (q,  $J = 7.1$  Hz, 2H), 2.42 (s, 3H), 1.84 (s, 3H), 1.23 (t,  $J = 7.1$  Hz, 3H);  $^{13}\text{C}$



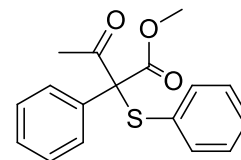
NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  169.7, 156.0, 149.4, 136.6, 135.7, 124.2, 121.0, 65.7, 62.7,

26.3, 22.0, 14.1; IR (KBr,  $\nu / \text{cm}^{-1}$ ) 3011, 1724, 1559, 1468, 1107, 856; HRMS ( $\text{ESI}^+$ )

Calcd for C<sub>12</sub>H<sub>15</sub>NO<sub>3</sub>S (M+Na<sup>+</sup>) 276.0665, Found 276.0662.

**methyl 3-oxo-2-phenyl-2-(phenylthio)butanoate (3af):**

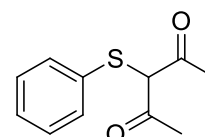
18.3 mg, 61%, colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.56 (dd, *J* = 6.5, 2.9 Hz, 2H), 7.38 – 7.30 (m, 7H), 7.21 – 7.15 (m, 2H), 3.72 (s, 3H), 1.66 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 167.8,



137.9, 135.3, 132.7, 129.9, 129.3, 129.1, 128.5, 127.6, 52.1, 22.5; IR (KBr, ν / cm<sup>-1</sup>) 3058, 2955, 1724, 1554, 1197, 730; HRMS (ESI<sup>+</sup>) Calcd for C<sub>17</sub>H<sub>16</sub>O<sub>3</sub>S (M+Na<sup>+</sup>) 323.0712, Found 323.0716.

**3-(phenylthio)pentane-2,4-dione (3ag):**

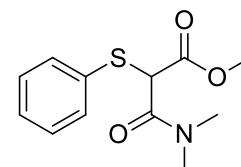
17.7 mg, 85%, colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.28 (t, *J* = 7.7 Hz, 2H), 7.17 – 7.06 (m, 3H), 2.34 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 198.5, 137.9, 129.4, 125.4, 124.9, 101.8, 24.6; IR



(KBr, ν / cm<sup>-1</sup>) 3062, 1703, 1582, 1478, 1023, 740, 691; HRMS (ESI<sup>+</sup>) Calcd for C<sub>11</sub>H<sub>12</sub>O<sub>2</sub>S (M+Na<sup>+</sup>) 231.0450, Found 231.0451.

**methyl 3-(dimethylamino)-3-oxo-2-(phenylthio)propanoate (3ah):**

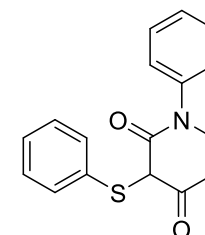
20.0 mg, 79%, colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.51 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.32 (dd, *J* = 4.9, 1.7 Hz, 3H), 4.77 (s, 1H), 3.77 (s, 3H), 3.02 (s, 3H), 2.96 (s, 3H); <sup>13</sup>C NMR (100 MHz,



CDCl<sub>3</sub>) δ 168.1, 165.4, 133.3, 132.9, 129.3, 128.7, 55.3, 53.4, 38.0, 36.4; IR (KBr, ν / cm<sup>-1</sup>) 2954, 1737, 1655, 1398, 1157, 747; HRMS (ESI<sup>+</sup>) Calcd for C<sub>12</sub>H<sub>15</sub>NO<sub>3</sub>S (M+Na<sup>+</sup>) 276.0665, Found 276.0660.

**methyl 3-(methyl(phenyl)amino)-3-oxo-2-(phenylthio)propanoate (3ai):**

25.5 mg, 81%, colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.36 (t, *J* = 7.3 Hz, 3H), 7.21 (s, 6H), 7.13 (d, *J* = 7.8 Hz, 2H), 4.38 (s, 1H), 3.31 (s, 3H), 2.30 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 201.3, 166.3, 142.9, 133.2, 132.4, 130.2, 129.4, 128.8, 128.4, 127.7, 61.2,

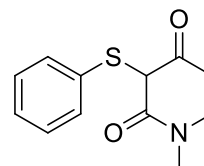




38.2, 27.5; IR (KBr,  $\nu / \text{cm}^{-1}$ ) 2968, 1742, 1638, 1209, 731; HRMS (ESI<sup>+</sup>) Calcd for C<sub>17</sub>H<sub>17</sub>NO<sub>3</sub>S (M+Na<sup>+</sup>) 338.0821, Found 338.0822.

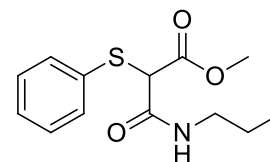
**N,N-dimethyl-3-oxo-2-(phenylthio)butanamide (3aj):**

19.0 mg, 80%, colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.42 – 7.36 (m, 2H), 7.30 (dd,  $J = 7.7, 5.9$  Hz, 3H), 4.69 (s, 1H), 3.05 (s, 3H), 3.00 (s, 3H), 2.40 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  201.7, 165.6, 133.3, 132.0, 129.5, 128.3, 77.2, 62.8, 38.0, 36.4, 26.3; IR (KBr,  $\nu / \text{cm}^{-1}$ ) 2956, 1732, 1641, 1204, 728; HRMS (ESI<sup>+</sup>) Calcd for C<sub>12</sub>H<sub>15</sub>NO<sub>2</sub>S (M+Na<sup>+</sup>) 260.0716, Found 260.0719.



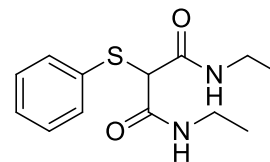
**methyl 3-oxo-2-(phenylthio)-3-(propylamino)propanoate (3ak):**

21.4 mg, 80%, white powder; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.48 – 7.42 (m, 2H), 7.36 – 7.30 (m, 3H), 6.95 (s, 1H), 4.37 (s, 1H), 3.76 (s, 3H), 3.24 – 3.16 (m, 2H), 1.47 (dd,  $J = 14.6, 7.3$  Hz, 2H), 0.86 (t,  $J = 7.4$  Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  169.4, 164.9, 132.8, 132.1, 129.5, 129.0, 55.0, 53.4, 41.9, 22.7, 11.4; IR (KBr,  $\nu / \text{cm}^{-1}$ ) 3299, 2963, 1739, 1659, 1441, 1262, 1156, 746, 691; HRMS (ESI<sup>+</sup>) Calcd for C<sub>13</sub>H<sub>17</sub>NO<sub>3</sub>S (M+Na<sup>+</sup>) 290.0821, Found 290.0824.



**N1,N3-diethyl-2-(phenylthio)malonamide (3al):**

18.4 mg, 69%, white powder; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.44 – 7.36 (m, 2H), 7.30 (dd,  $J = 9.8, 4.9$  Hz, 3H), 7.03 (s, 2H), 4.35 (s, 1H), 3.32 – 3.19 (m, 4H), 1.08 (t,  $J = 7.3$  Hz, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  166.8, 133.9, 132.9, 132.0, 129.4, 129.0, 128.3, 57.3, 57.3, 35.1, 14.5; IR (KBr,  $\nu / \text{cm}^{-1}$ ) 3310, 3347, 1649, 1524, 1441, 751; HRMS (ESI<sup>+</sup>) Calcd for C<sub>13</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>S (M+Na<sup>+</sup>) 289.0981, Found 289.0974.



**2-(phenylthio)malonamide (3am):**

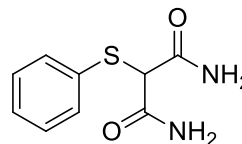
15.1 mg, 72%, white powder;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52

– 7.45 (m, 2H), 7.33 (dd,  $J = 5.0, 1.9$  Hz, 3H), 6.36 (s, 1H), 5.42

(s, 1H), 4.83 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.0, 132.9,

132.6, 129.5, 128.8, 58.2; IR (KBr,  $\nu / \text{cm}^{-1}$ ) 3362, 1657, 1493, 1271, 740; HRMS ( $\text{ESI}^+$ )

Calcd for  $\text{C}_9\text{H}_{10}\text{N}_2\text{O}_2\text{S}$  ( $\text{M}+\text{Na}^+$ ) 233.0355, Found 233.0357.



**dimethyl 2-methyl-2-(phenylthio)malonate (4):**

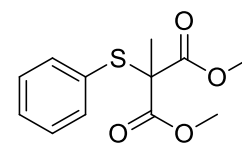
23.9 mg, 94%, colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 –

7.50 (m, 2H), 7.43 – 7.37 (m, 1H), 7.33 (t,  $J = 7.3$  Hz, 2H), 3.74

(s, 6H), 1.64 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  169.8, 137.4,

130.2, 129.8, 129.0, 60.2, 53.3, 22.6; IR (KBr,  $\nu / \text{cm}^{-1}$ ) 2954, 1735, 1441, 1262, 755,

695; HRMS ( $\text{ESI}^+$ ) Calcd for  $\text{C}_{12}\text{H}_{14}\text{O}_4\text{S}$  ( $\text{M}+\text{Na}^+$ ) 277.0505, Found 277.0503.



**dimethyl 2-benzoyl-2-(phenylthio)malonate (5):**

28.9 mg, 84%, colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.12 (d,

$J = 7.3$  Hz, 2H), 7.63 (t,  $J = 7.2$  Hz, 1H), 7.55 (d,  $J = 7.0$  Hz, 2H),

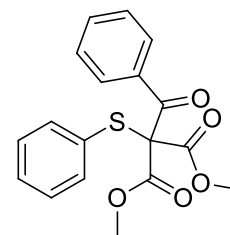
7.49 (t,  $J = 7.7$  Hz, 3H), 7.40 (dd,  $J = 14.9, 7.1$  Hz, 3H), 3.72 (s,

3H), 3.69 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.4, 163.6,

163.0, 160.0, 134.1, 133.7, 131.3, 130.5, 128.9, 128.7, 128.1,

118.2, 53.7, 52.9, 52.7; IR (KBr,  $\nu / \text{cm}^{-1}$ ) 2956, 1723, 1540, 1244, 722, 691; HRMS

( $\text{ESI}^+$ ) Calcd for  $\text{C}_{18}\text{H}_{16}\text{O}_5\text{S}$  ( $\text{M}+\text{Na}^+$ ) 367.0611, Found 367.0608.



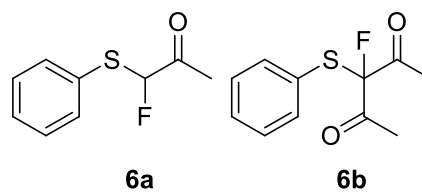
**1-fluoro-1-(phenylthio)propan-2-one (6a); 3-fluoro-3-(phenylthio)pentane-2,4-dione (6b):**

Total: 17.7 mg, **6a**, 19%; **6b**, 63%; colorless oil;  $^1\text{H}$

NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 – 7.51 (m, 2H),

7.42 – 7.32 (m, 3H), 6.06 (s, 1H), 5.93 (s, 1H), 2.22

(d,  $J = 3.5$  Hz, 1H), 2.13 (d,  $J = 2.8$  Hz, 2H);  $^{13}\text{C}$



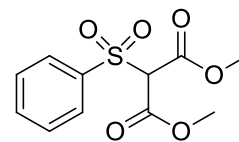
NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  199.8, 199.5, 197.7, 197.4, 135.9, 134.2, 134.2, 130.5, 129.7,

129.6, 129.5, 101.0, 98.6, 26.7, 26.3; IR (KBr,  $\nu / \text{cm}^{-1}$ ) 3453, 2928, 1730, 1440, 1359,

1180, 691; HRMS (ESI<sup>+</sup>) Calcd for C<sub>9</sub>H<sub>9</sub>FOS (M+Na<sup>+</sup>) 207.0250, Found 207.0249; HRMS (ESI<sup>+</sup>) Calcd for C<sub>11</sub>H<sub>11</sub>FO<sub>2</sub>S (M+Na<sup>+</sup>) 249.0356, Found 249.0359.

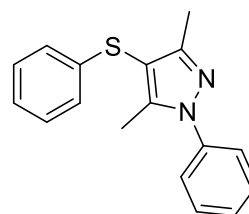
**dimethyl 2-(phenylsulfonyl)malonate (7):**

25.8 mg, 95%, colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.01 – 7.95 (m, 2H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.8 Hz, 2H), 5.01 (s, 1H), 3.78 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 161.5, 137.3, 135.0, 130.2, 129.1, 74.5, 53.9; IR (KBr, ν / cm<sup>-1</sup>) 2958, 1746, 1450, 1336, 1154, 1083, 688; HRMS (ESI<sup>+</sup>) Calcd for C<sub>11</sub>H<sub>12</sub>O<sub>6</sub>S (M+Na<sup>+</sup>) 295.0247, Found 295.0251.



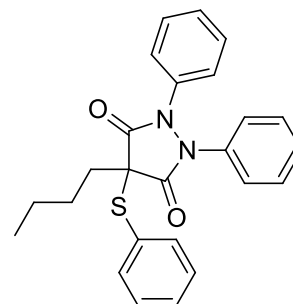
**3,5-dimethyl-1-phenyl-4-(phenylthio)-1H-pyrazole (8):**

25.8 mg, 92%, colorless oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.49 (d, *J* = 4.3 Hz, 4H), 7.43 – 7.36 (m, 1H), 7.24 (dd, *J* = 10.2, 4.8 Hz, 2H), 7.14 – 7.04 (m, 3H), 2.35 (s, 3H), 2.31 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 153.3, 144.3, 139.8, 138.4, 129.3, 129.0, 128.0, 125.4, 125.0, 124.8, 106.1, 12.2, 11.7; IR (KBr, ν / cm<sup>-1</sup>) 3058, 1579, 1582, 1504, 1478, 1023, 734, 690, HRMS (ESI<sup>+</sup>) Calcd for C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>S (M+Na<sup>+</sup>) 303.0926, Found 303.0928.

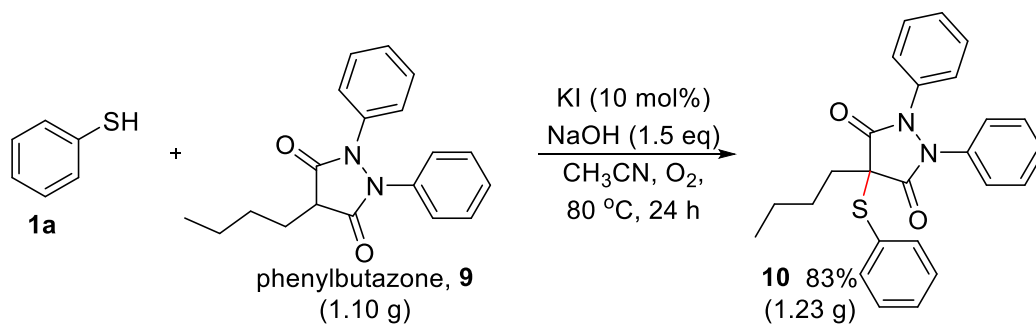


**4-butyl-1,2-diphenyl-4-(phenylthio)pyrazolidine-3,5-dione (10):**

1.23 g (gram scale experiment), 83%, faint yellow solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.57 (d, *J* = 7.1 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 7.7 Hz, 2H), 7.15 (t, *J* = 7.5 Hz, 4H), 7.08 (t, *J* = 7.3 Hz, 2H), 6.80 (d, *J* = 7.4 Hz, 4H), 2.21 – 2.09 (m, 2H), 1.36 (dd, *J* = 19.7, 16.0 Hz, 4H), 0.87 (t, *J* = 6.9 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 169.7, 137.4, 134.9, 130.6, 129.6, 128.9, 128.4, 127.1, 123.1, 59.0, 33.5, 27.4, 22.8, 13.8; IR (KBr, ν / cm<sup>-1</sup>) 2961, 2927, 1754, 1724, 1597, 1491, 1292, 755, 693; HRMS (ESI<sup>+</sup>) Calcd for C<sub>25</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>S (M+Na<sup>+</sup>) 439.1451, Found 439.1452.



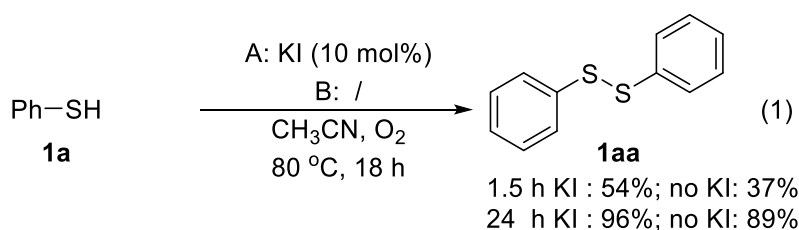
### Scheme S1. Gram scale experiments.



A gram-scale experiment was carried out under standard condition: a round flask equipped with a magnetic stir bar was charged with thiol **1a** (0.6 g, 1.5 eq), Phenylbutazone **9** (1.1 g, 1.0 eq), KI (60 mg), NaOH (0.22 g, 1.5 eq), CH<sub>3</sub>CN (15 ml). The resulting mixture was stirred at room temperature for 15 min, then the temperature was elevated to 80 °C slowly and stirred for 24 h, then quenched by saturated NaHCO<sub>3</sub> aqueous solution, and extracted with ethyl acetate (3\*50mL), the combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel (hexane / EtOAc = 20 : 1) to give **10** as faint yellow solid (1.23g, 83% yield).

### Scheme S2. Controlled experiments.

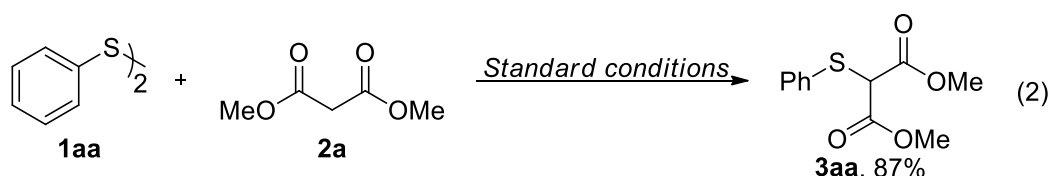
#### (a) Reaction in eq 1.



A test tube equipped with a magnetic stir bar was charged with thiophenol **1a** (0.10 mmol), KI (10 mol%) or not, CH<sub>3</sub>CN (1 mL) under O<sub>2</sub> atmosphere. The resulting mixture was stirred at 80 °C for 1.5 h and 24 h respectively, then the reaction solution

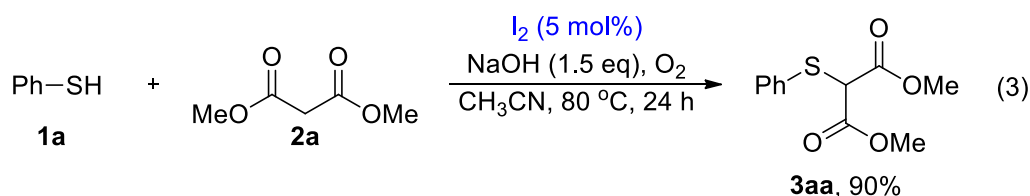
was concentrated and the resulting residue was purified by column chromatography on silica gel (hexane / EtOAc = 80:1) to give **1aa** as white crystal (yield was depicted in eq 1 respectively).

**(b) Reaction in eq 2.**



A test tube equipped with a magnetic stir bar was charged with 1,2-diphenyldisulfane **1aa** (0.05 mmol), dimethyl malonate **2a** (0.20 mmol), KI (10 mol%), NaOH (0.15 mmol) CH<sub>3</sub>CN (1 mL) under O<sub>2</sub> atmosphere. The resulting mixture was stirred at 80 °C for 24 h, then quenched by saturated NaHCO<sub>3</sub> aqueous solution, and extracted with ethyl acetate (3\*25mL), the combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel (hexane / EtOAc = 20:1) to give **3aa** as colorless oil (yield: 87%).

**(c) Reaction in eq 3.**



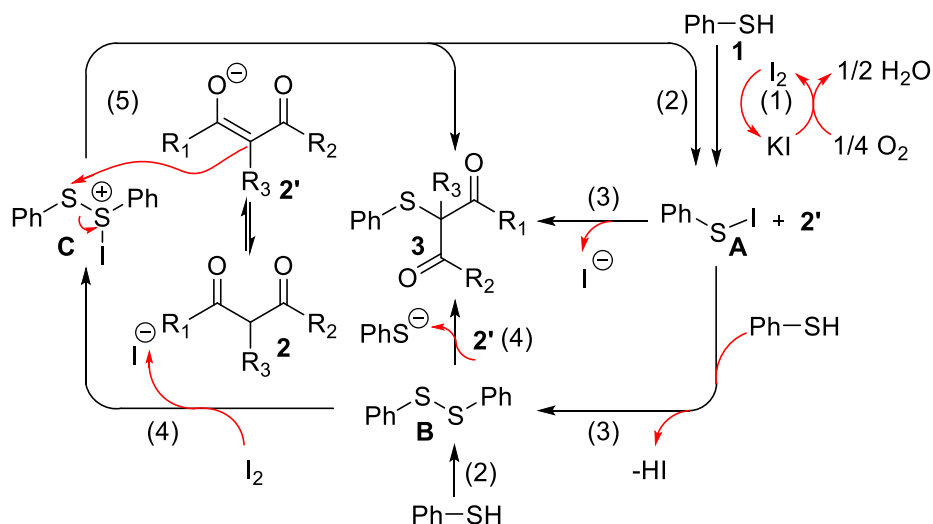
A test tube equipped with a magnetic stir bar was charged with thiophenol **1a** (0.10 mmol), dimethyl malonate **2a** (0.20 mmol), I<sub>2</sub> (5 mol%), NaOH (0.15 mmol) CH<sub>3</sub>CN (1 mL) under O<sub>2</sub> atmosphere. The resulting mixture was stirred at 80 °C for 24 h, then quenched by saturated NaHCO<sub>3</sub> aqueous solution, and extracted with ethyl acetate (3\*25mL), the combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel (hexane / EtOAc = 20:1) to give **3aa** as colorless oil (yield: 90%).

**(d) Reaction in eq 4.**



A test tube equipped with a magnetic stir bar was charged with thiophenol **1a** (0.10 mmol), dimethyl malonate **2a** (0.15 mmol), KI (10 mol%), NaOH (0.15 mmol), BHT or TEMPO (0.20 mmol) and CH<sub>3</sub>CN (1 mL) under O<sub>2</sub> atmosphere. The resulting mixture was stirred at 80 °C for 18 h, then quenched by saturated NaHCO<sub>3</sub> aqueous solution, and extracted with ethyl acetate (3\*25mL), the combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel (hexane / EtOAc = 20:1) to give **3aa** as colorless oil (yield: 85%).

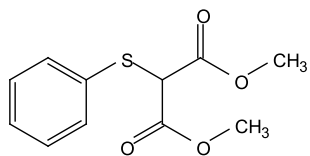
**Scheme S3.** A proposed mechanism.



The proposed mechanism as follows<sup>[4]</sup>: 1) Iodine ions (I<sup>-</sup>) was oxidized to iodine (I<sub>2</sub>) by oxygen molecule. 2) Nucleophilic thiol **1** attacked I<sub>2</sub> and generated the intermediate **A** as well as one molecule of I<sup>-</sup> through heterolysis, besides, the disulfide **B** could be directly formed by oxidation of thiol under the oxygen atmosphere. 3) The intermediate **A** was attacked by the enolate **2'** formed the final product **3**, alternatively, disulfide was yielded. 4) An activated transition state **C** was provided through oxidizing the disulfide with I<sub>2</sub>, meanwhile, the final product could be generated as well, from the enolate **2'** nucleophilic attacked **B**. 5) Intermediate **C** was then converted to the desired product by a direct nucleophilic substitution and released one molecule of intermediate **A**.

## References:

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2. L.-S. Ge, Z.-L. Wang, X.-L. An, X. Luo and W.-P. Deng, *Org. Biomol. Chem.*, 2014, **12**, 8473.
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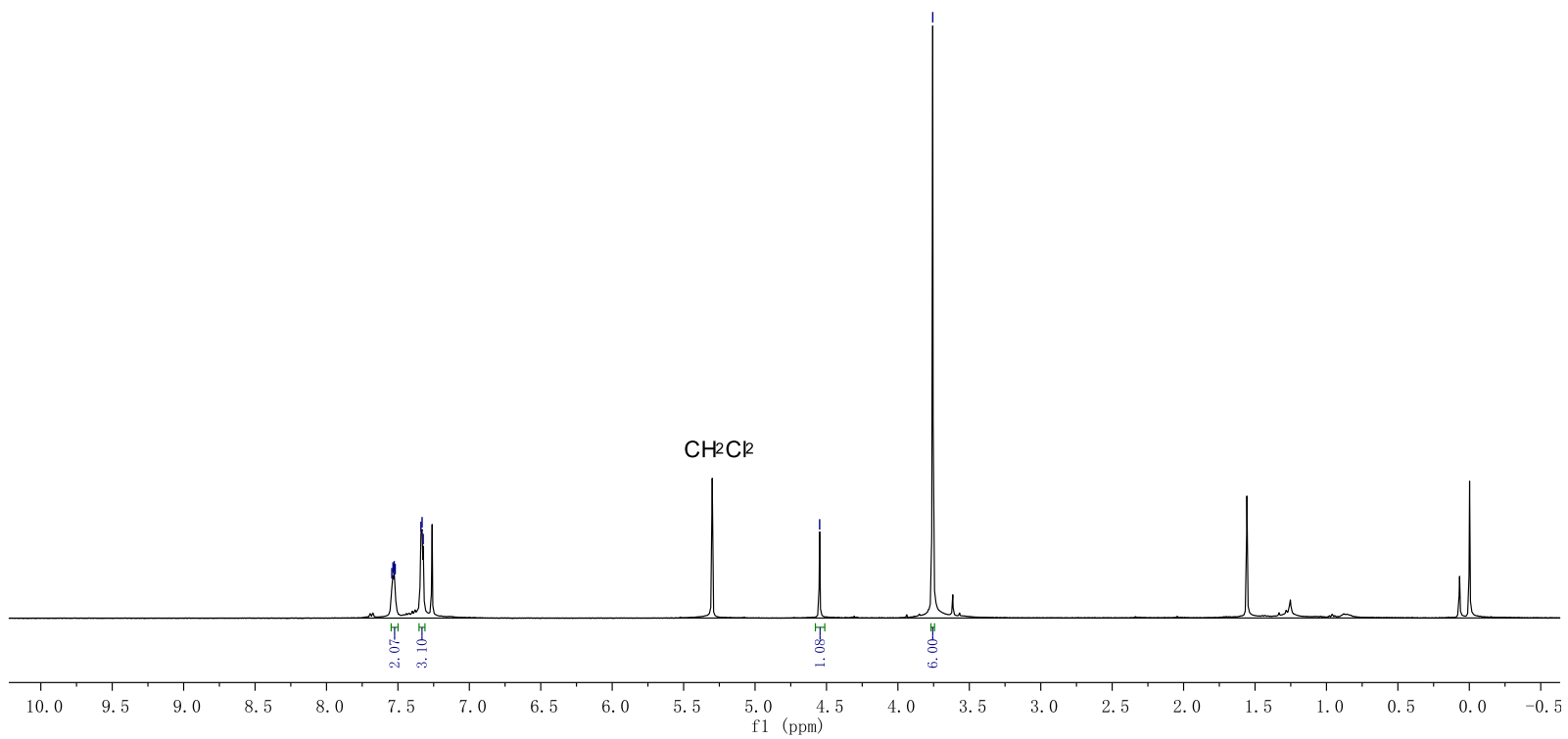


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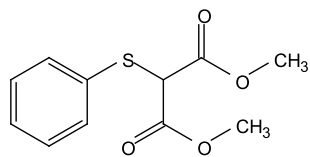
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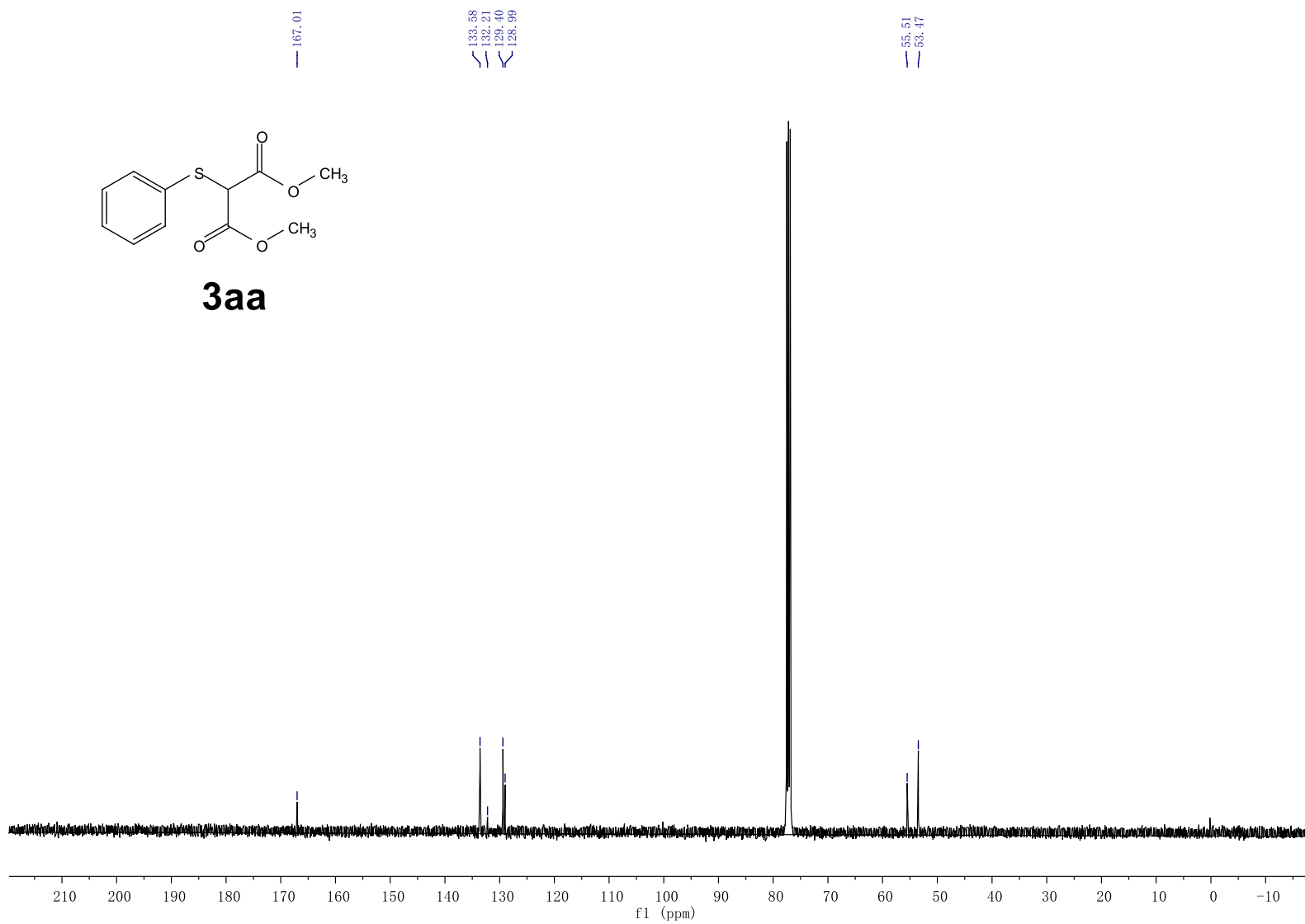
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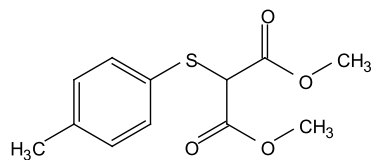




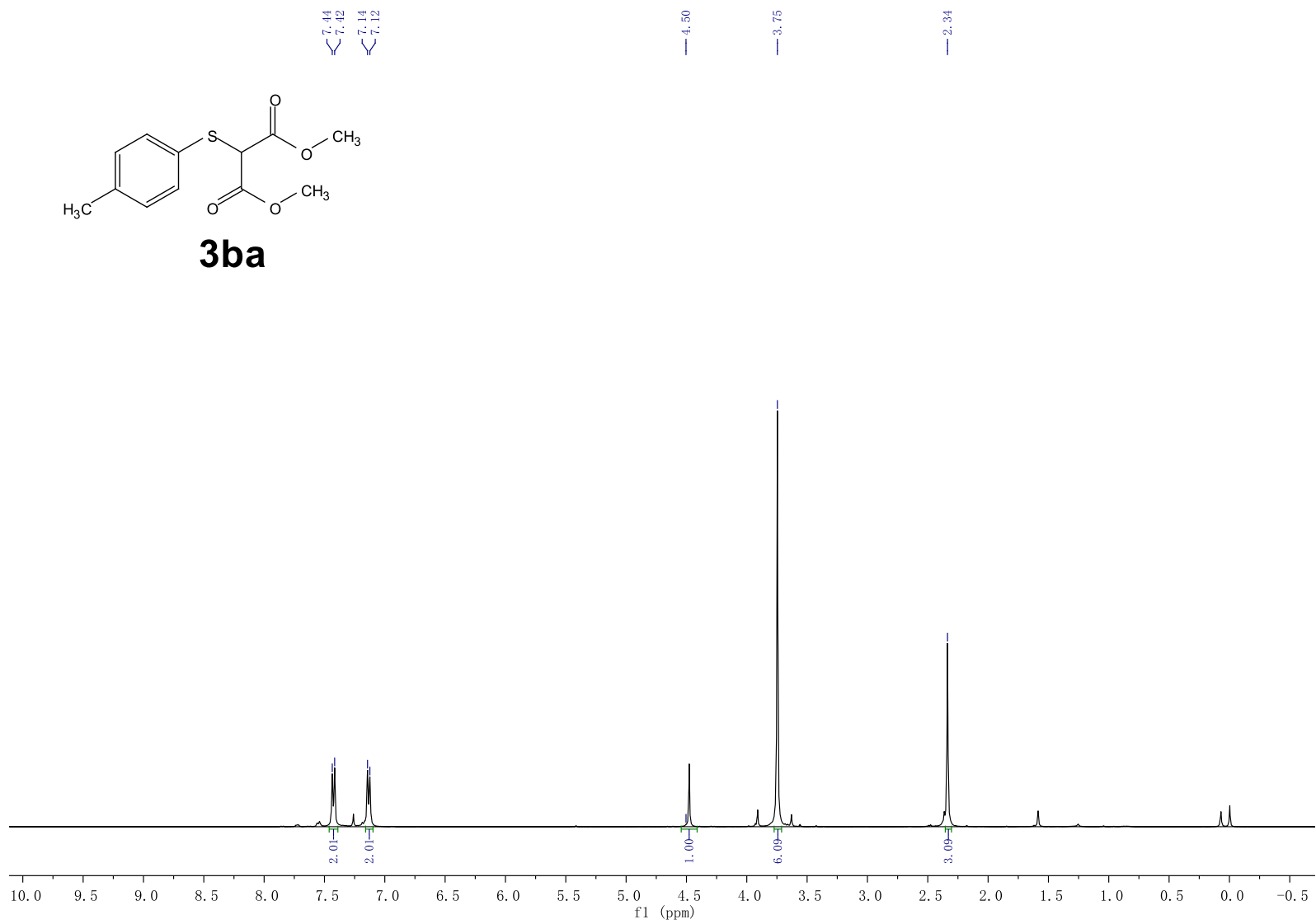


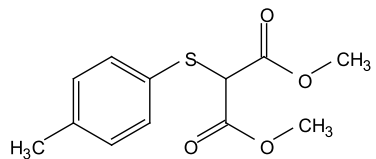
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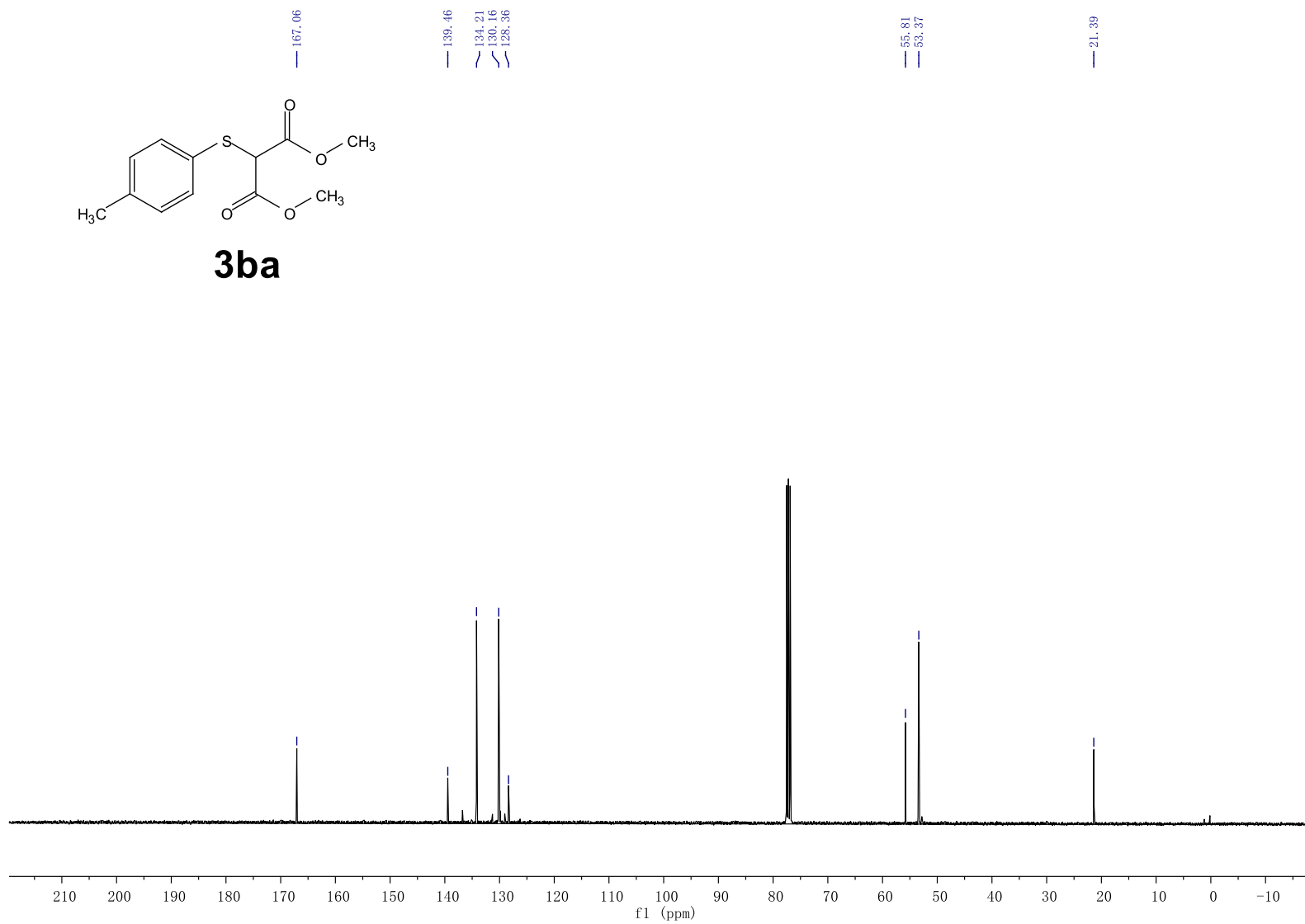


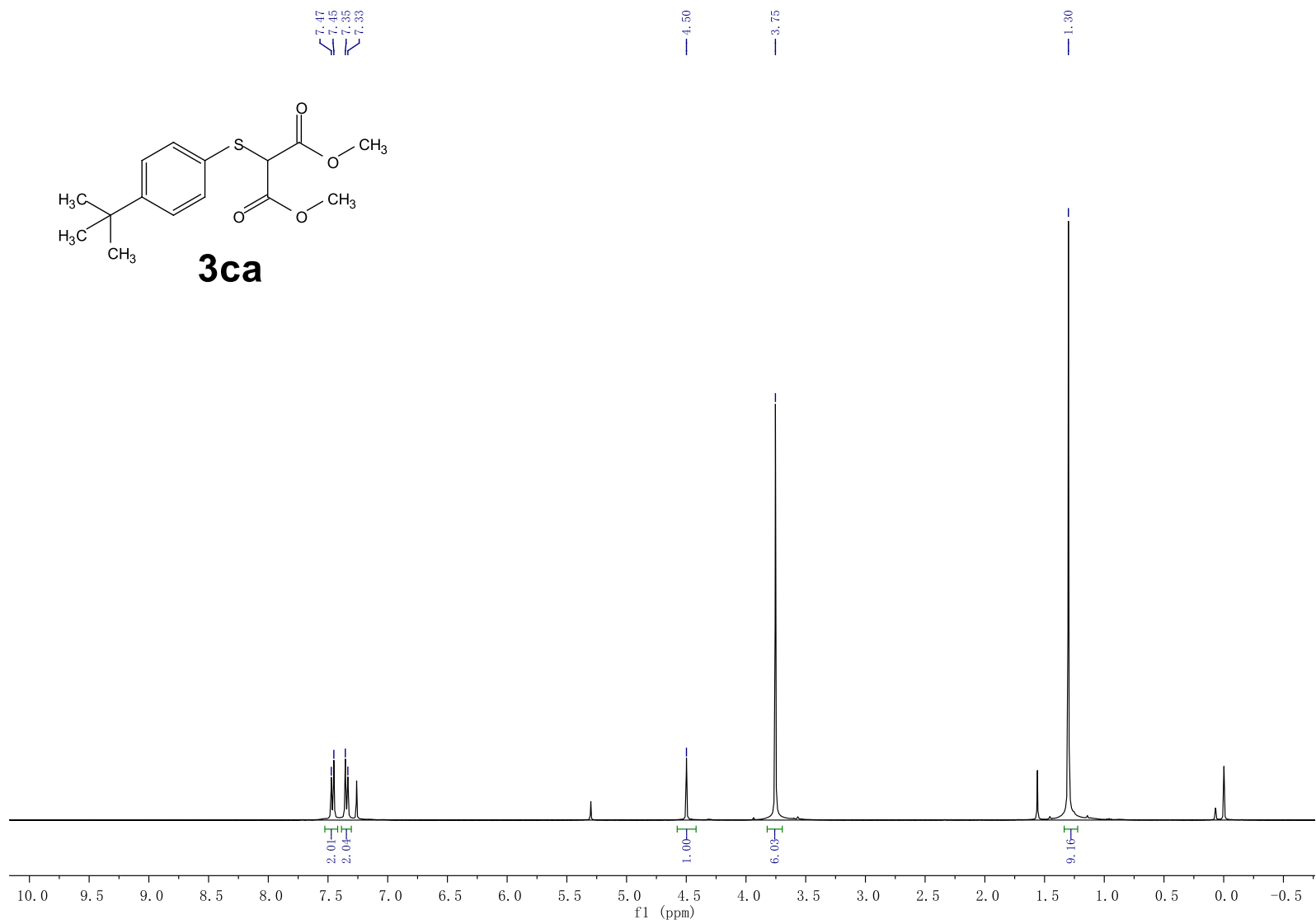
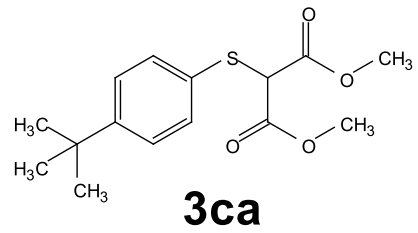
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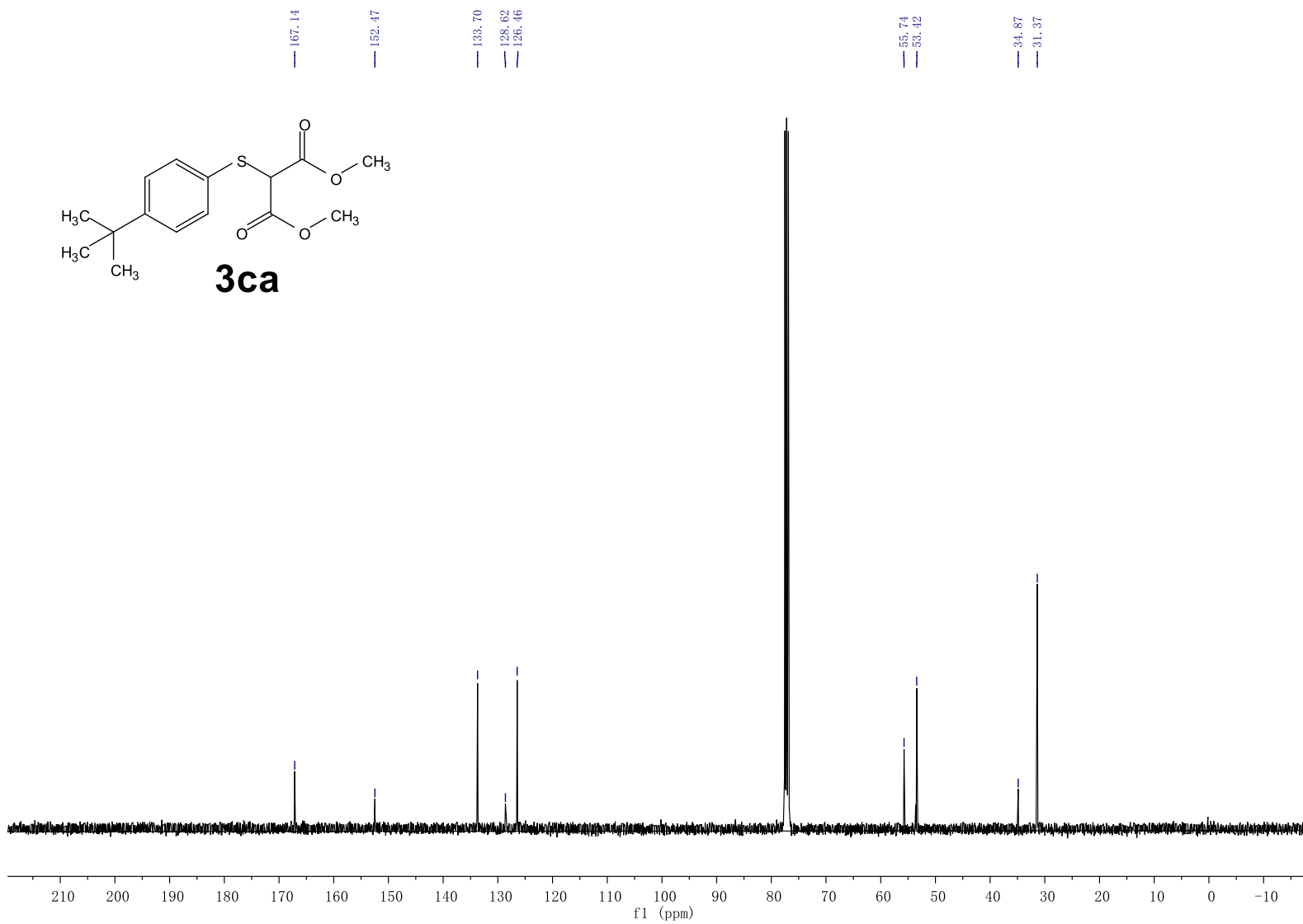
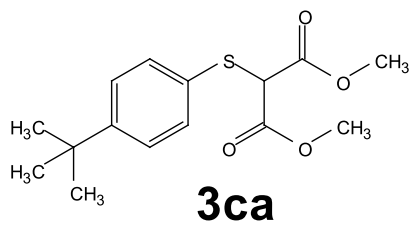


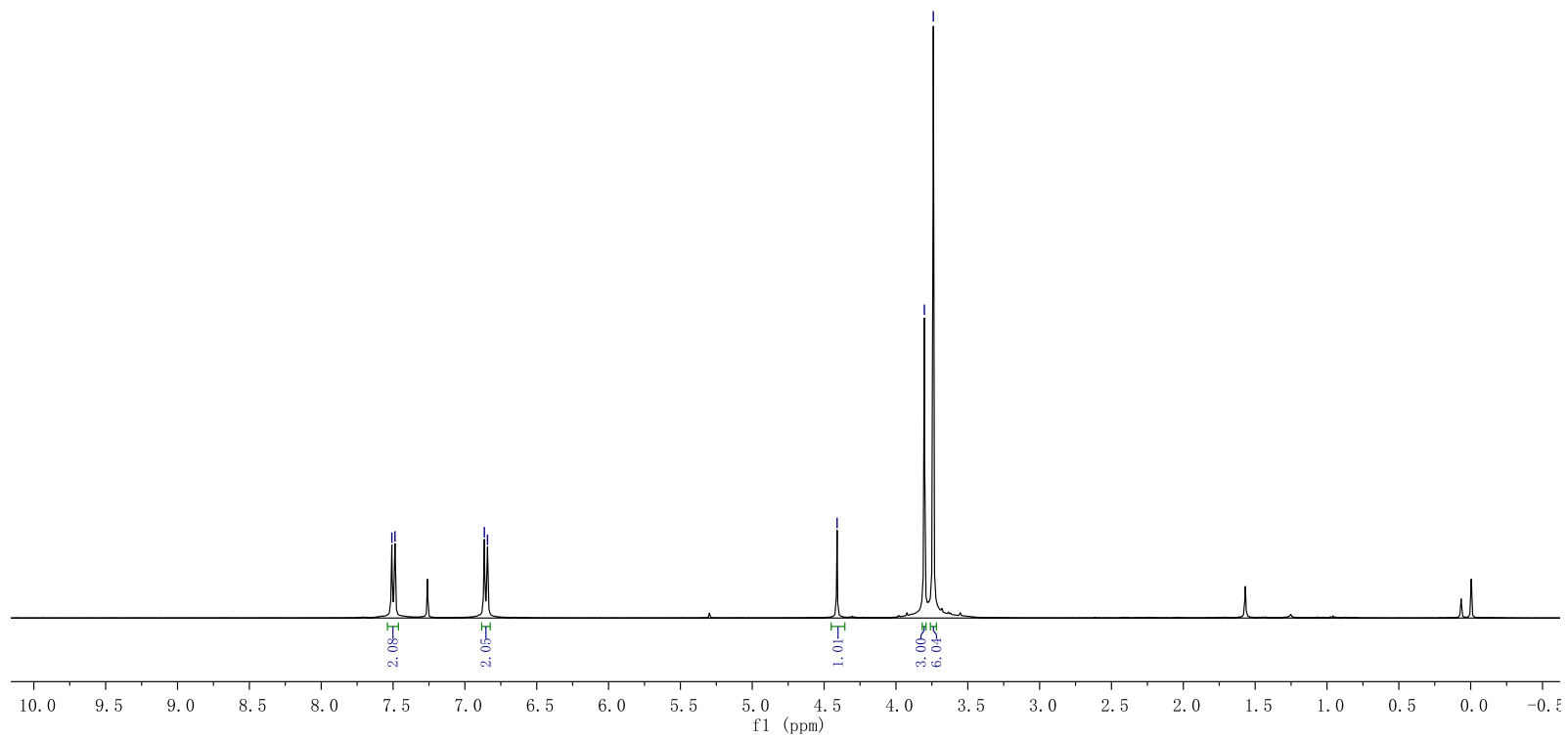
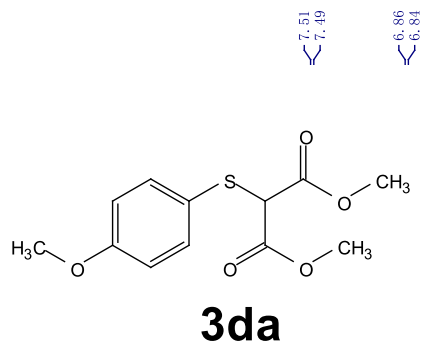


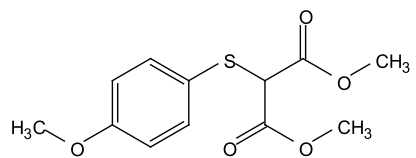
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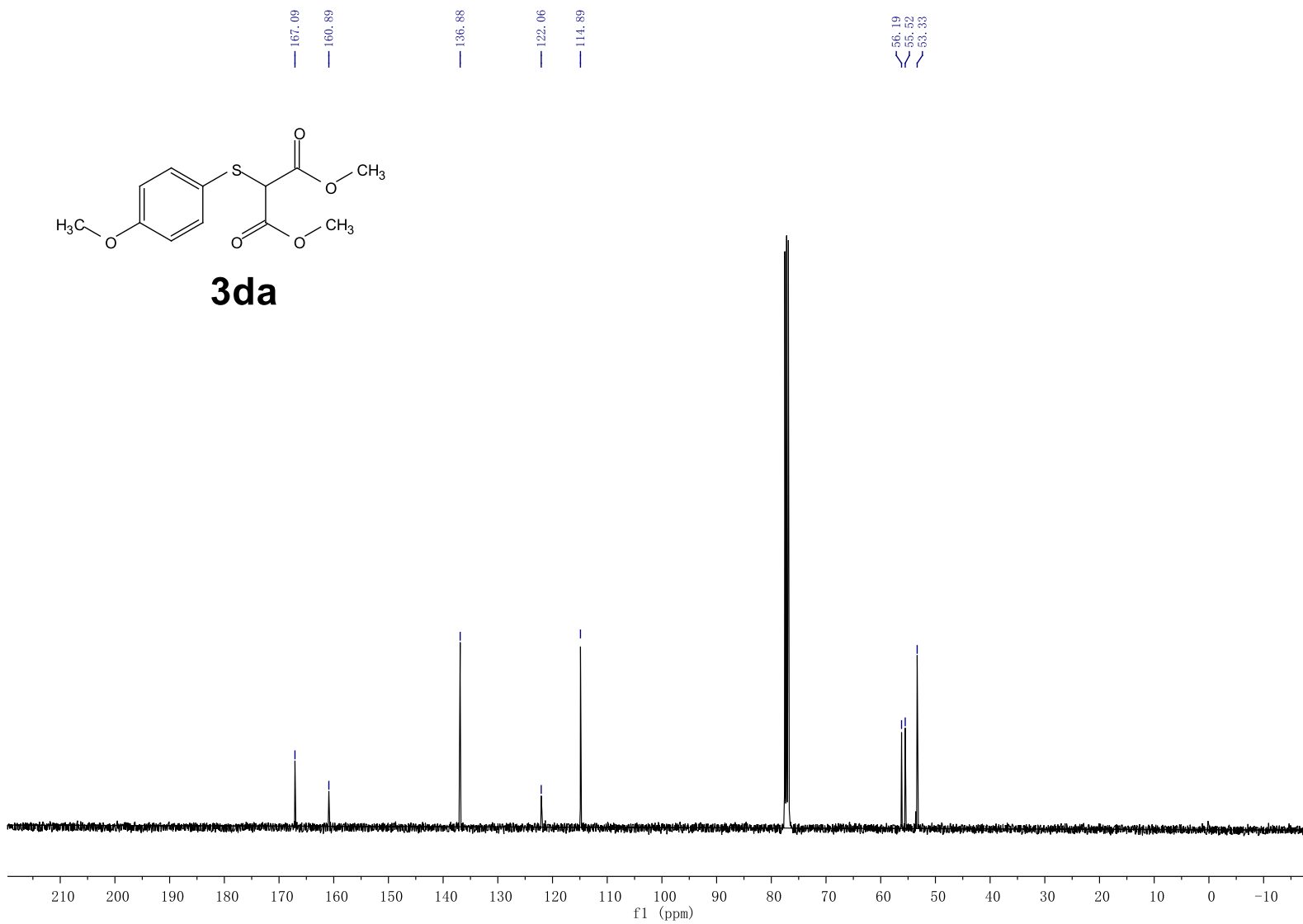


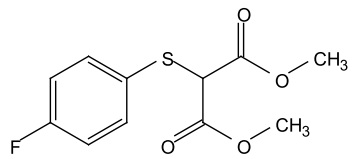






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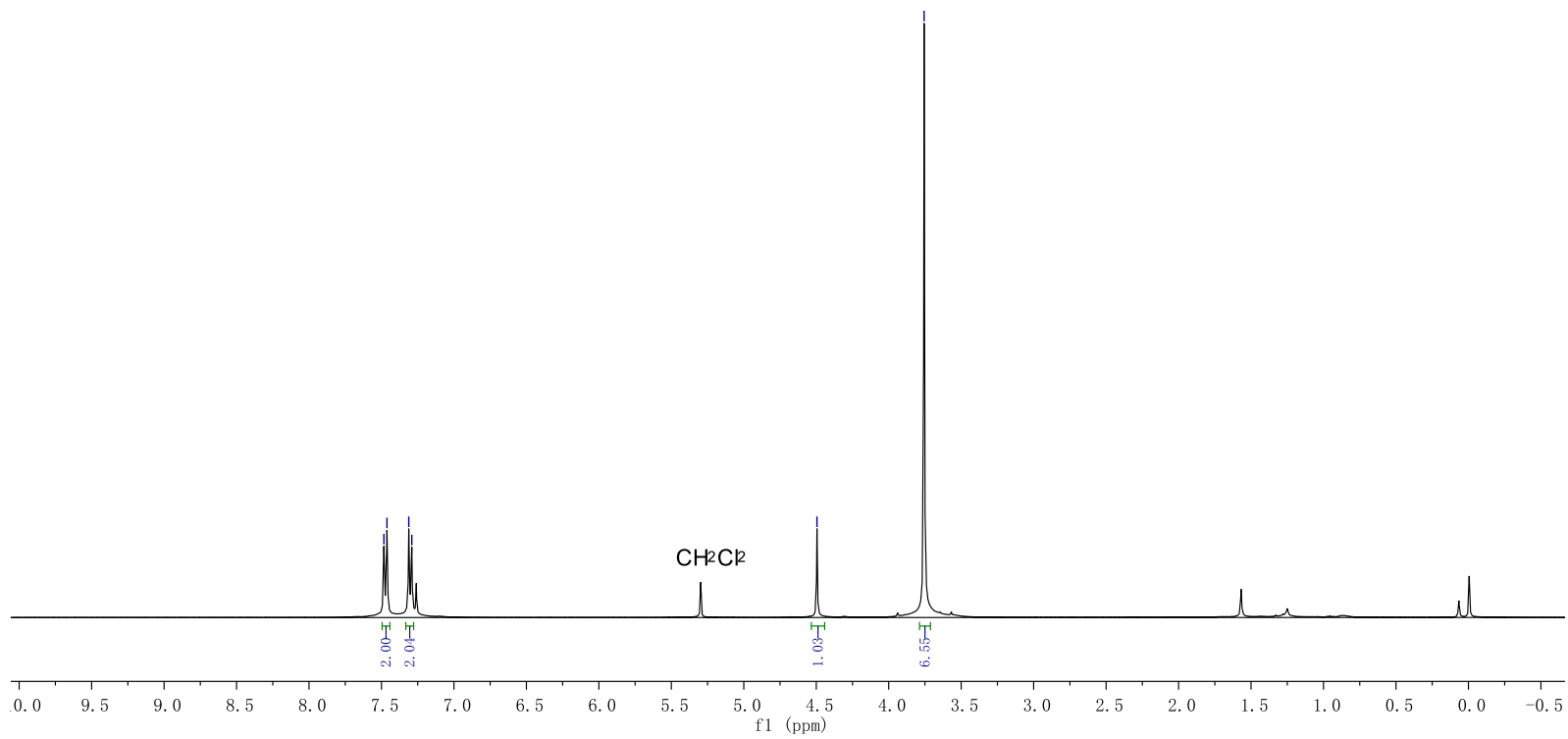


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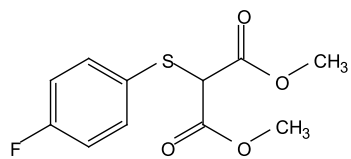
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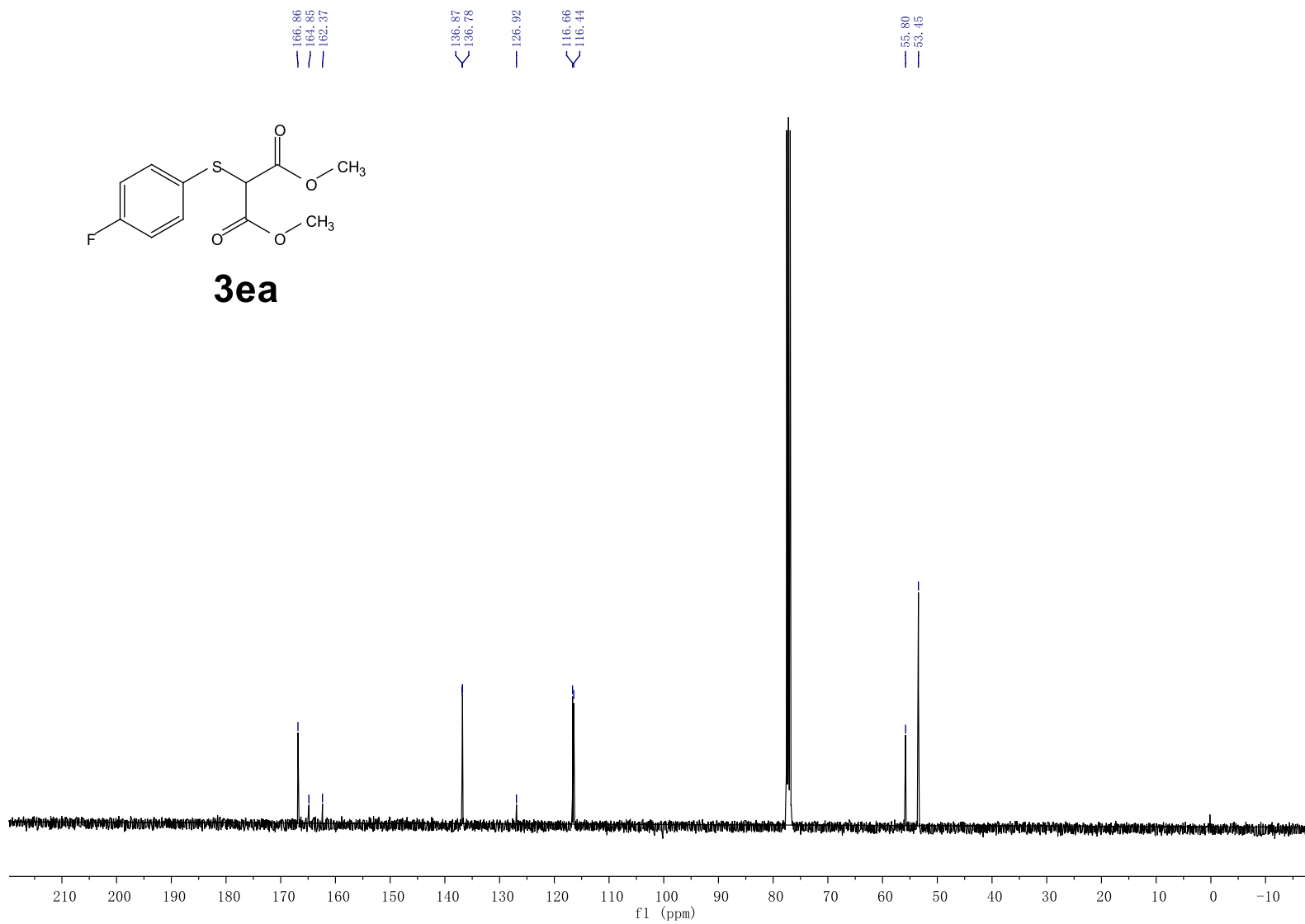
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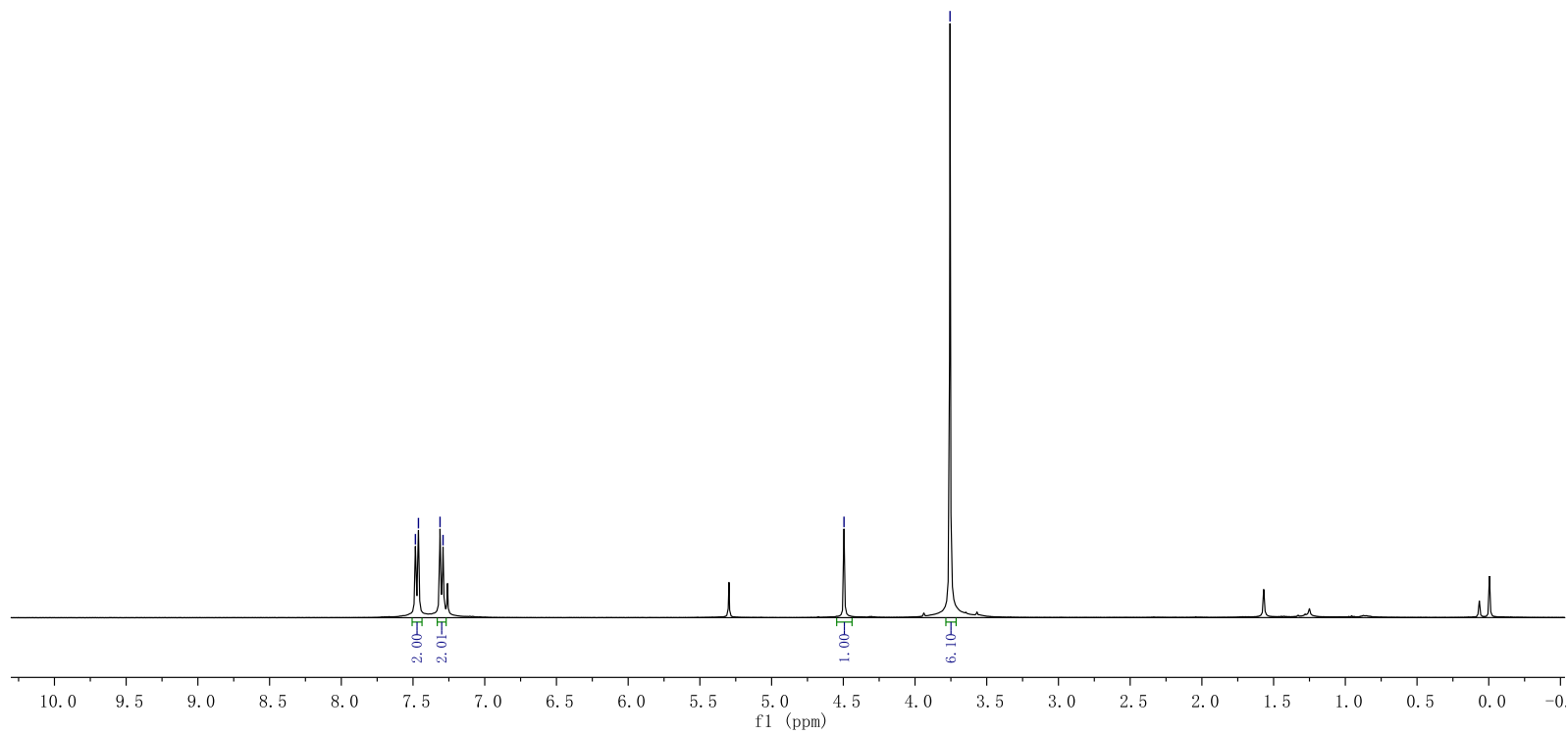
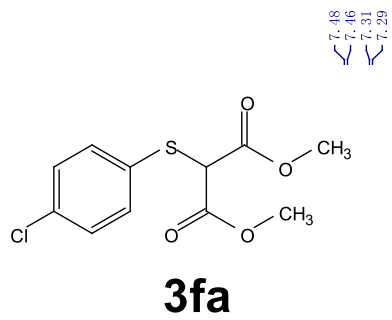


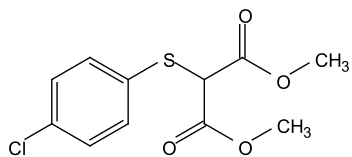




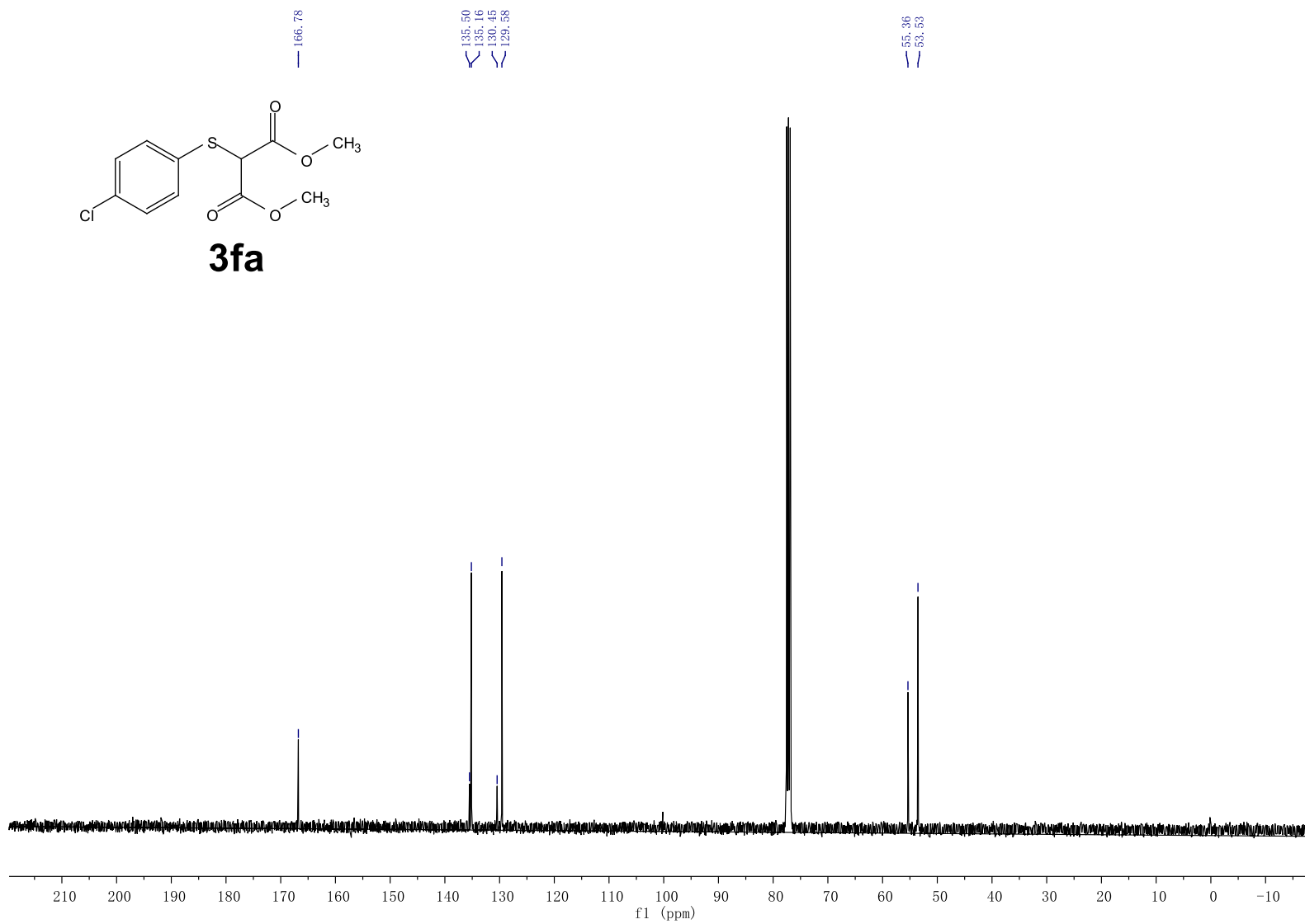
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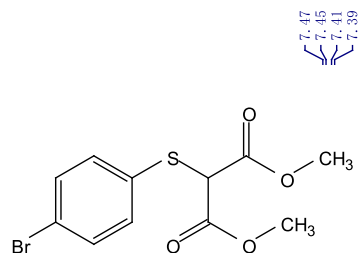




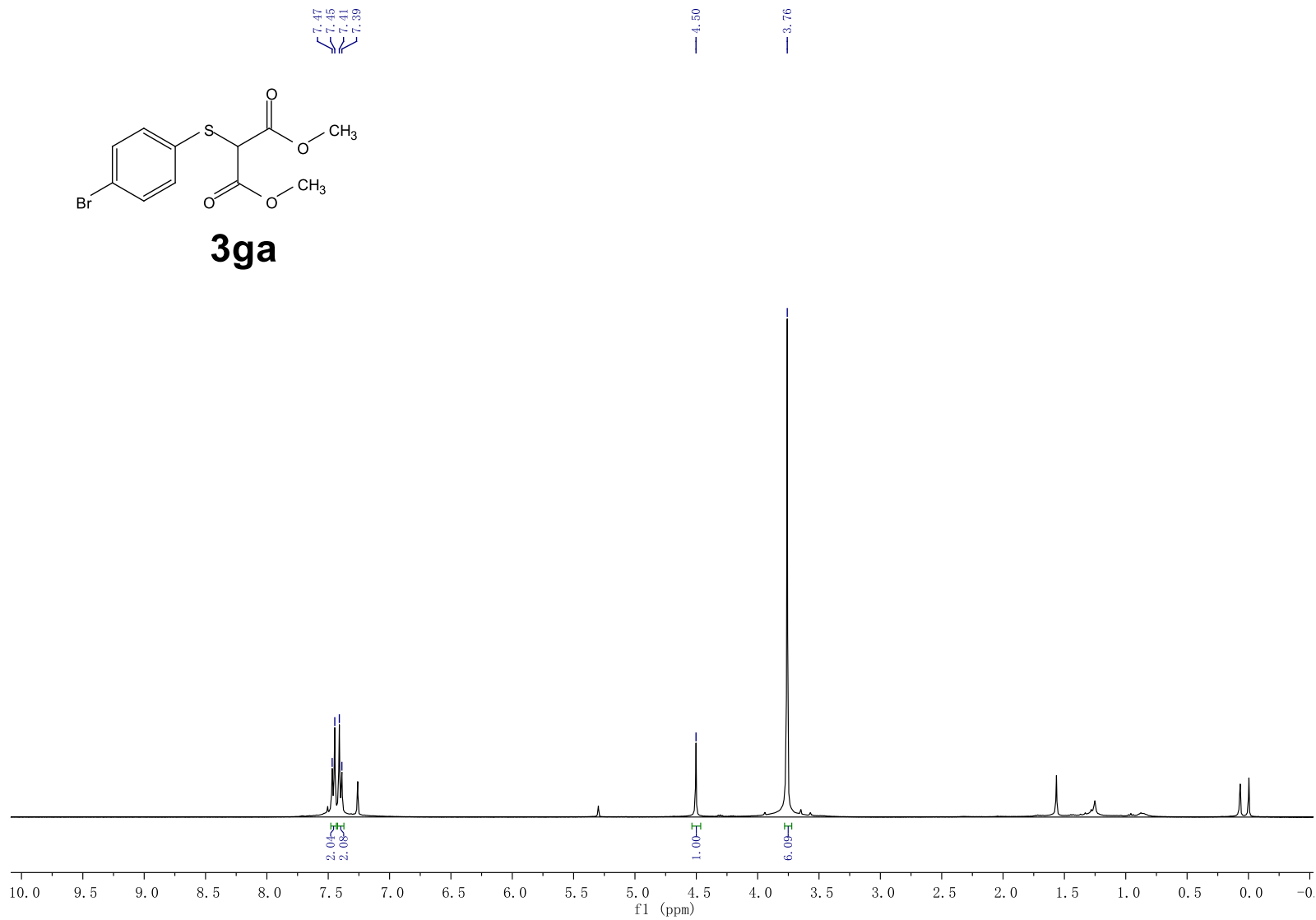


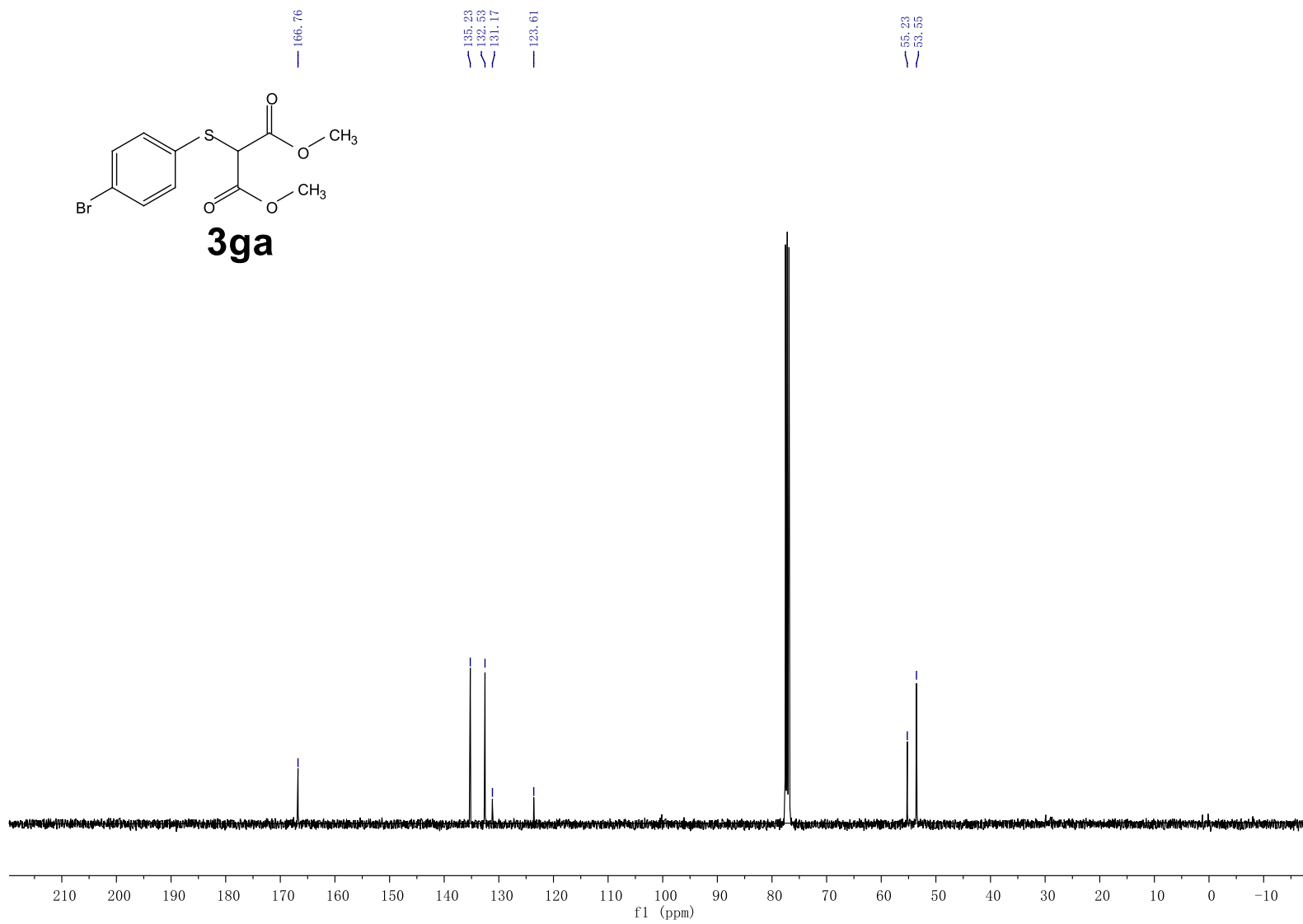
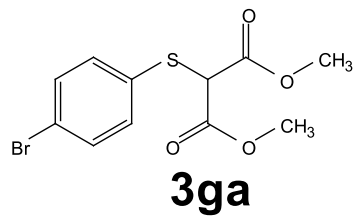
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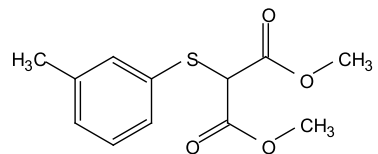




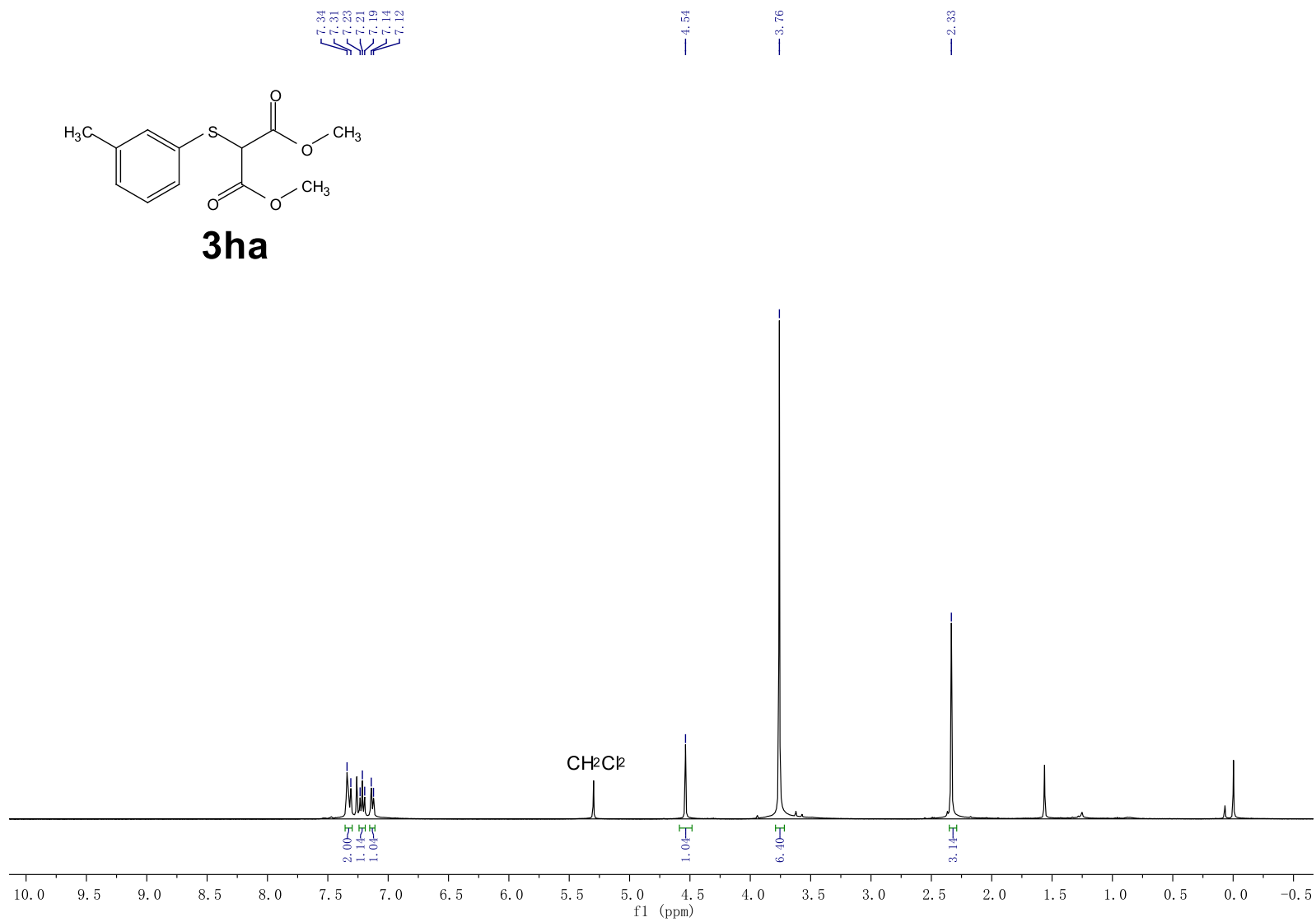
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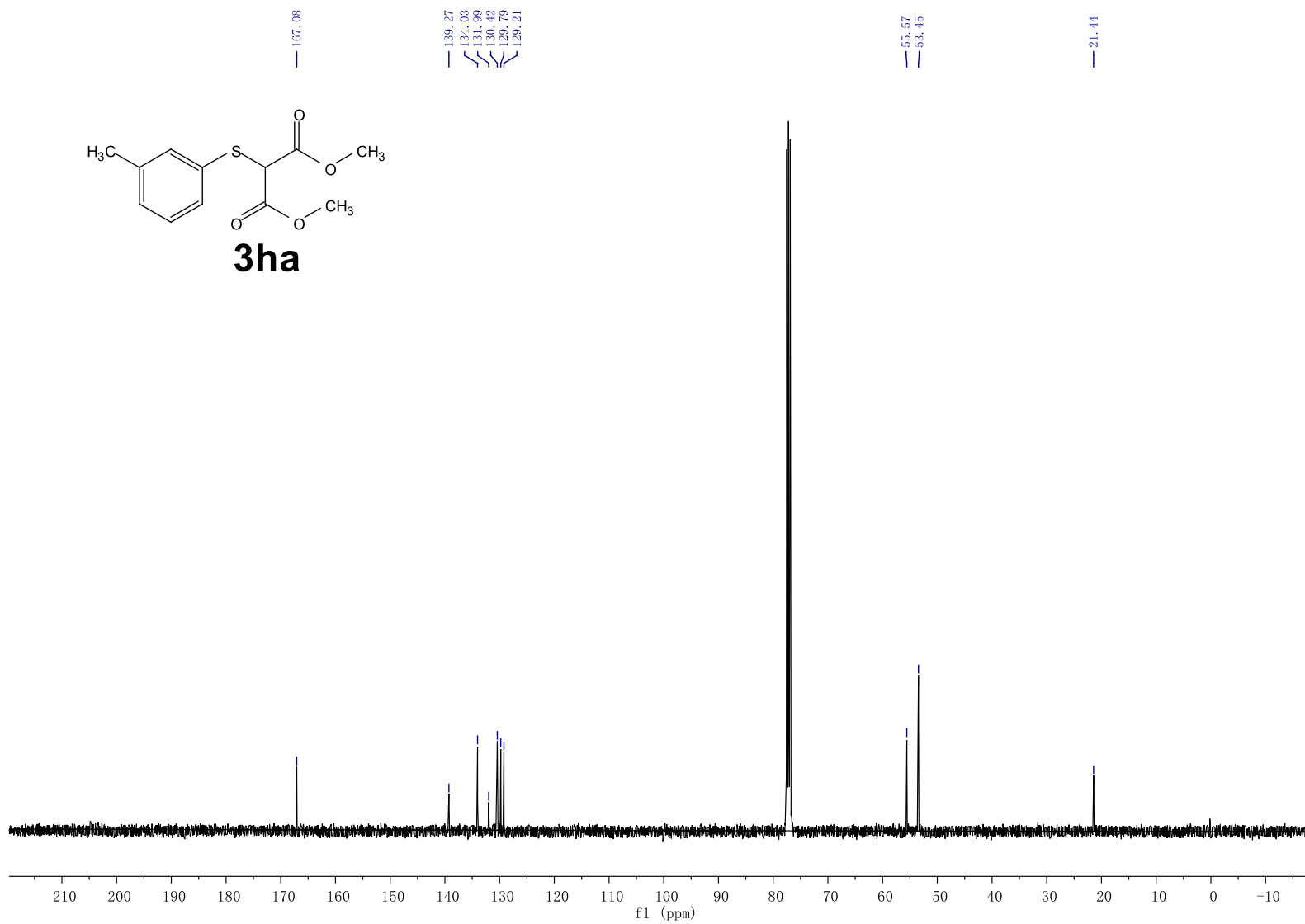
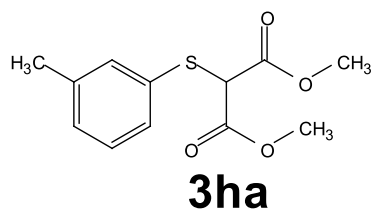


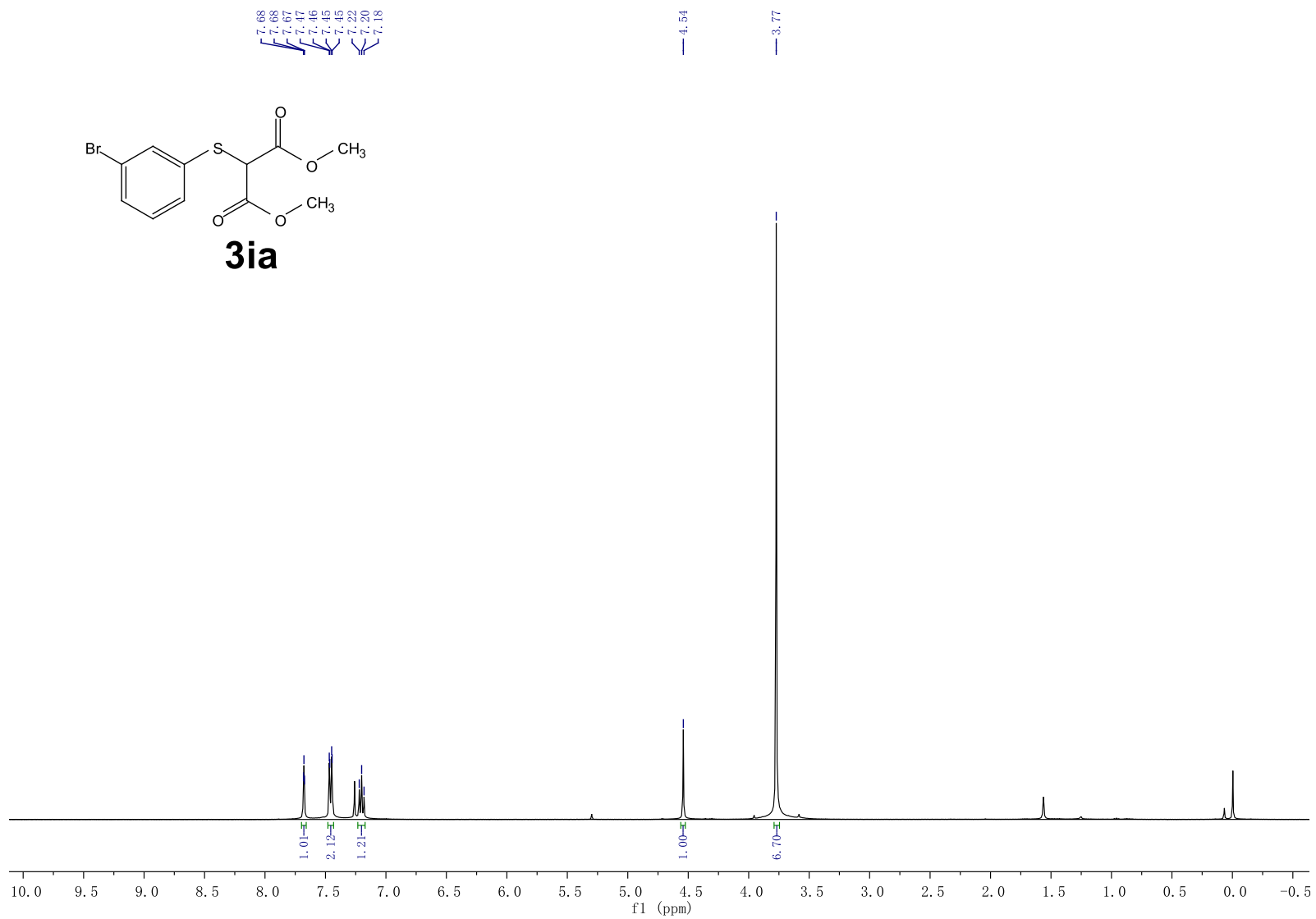
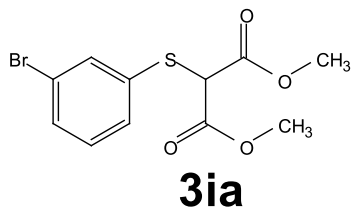




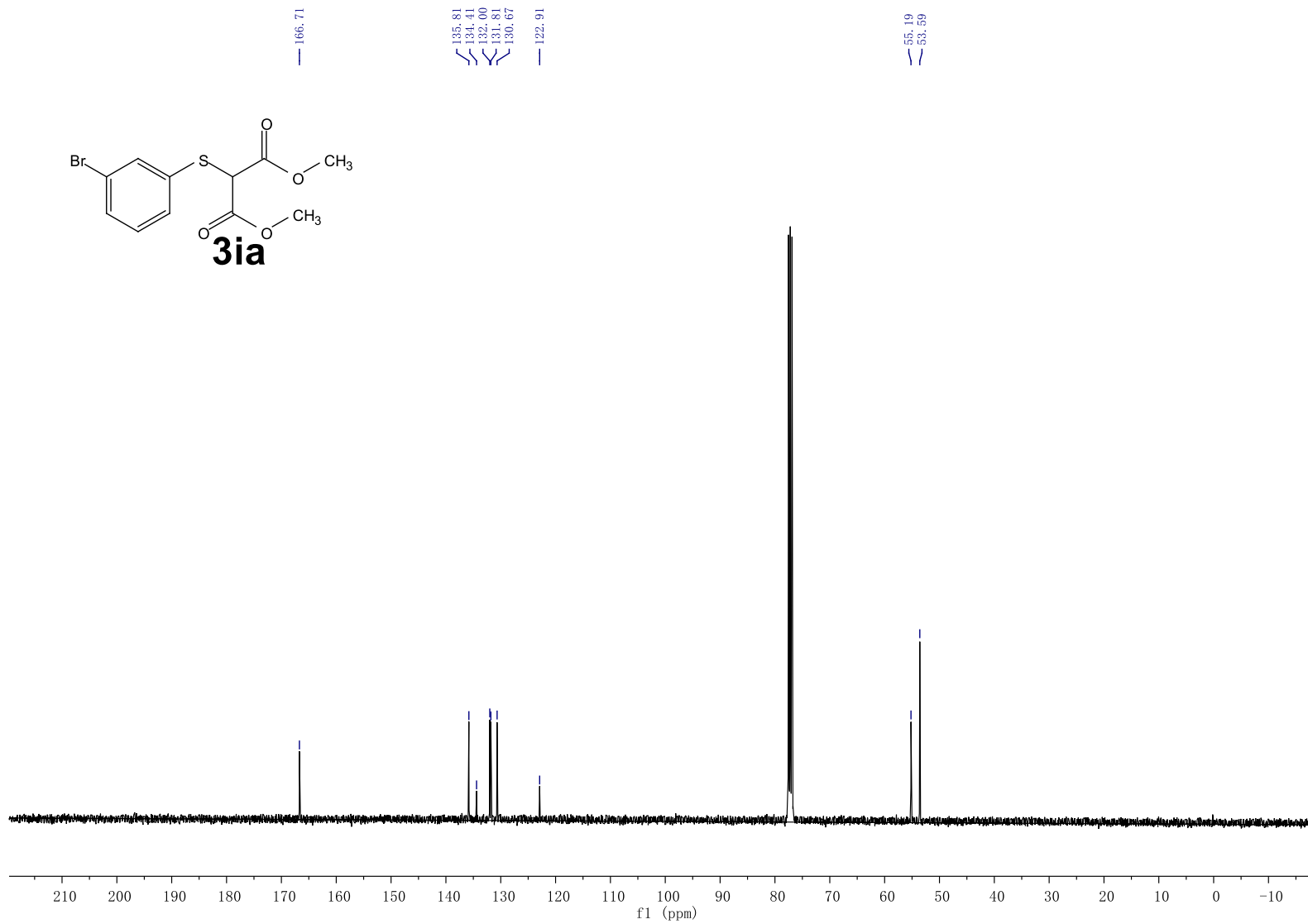
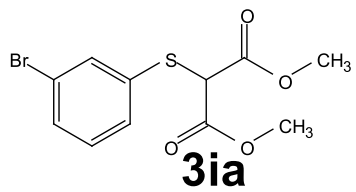
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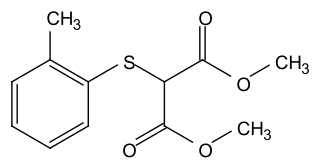




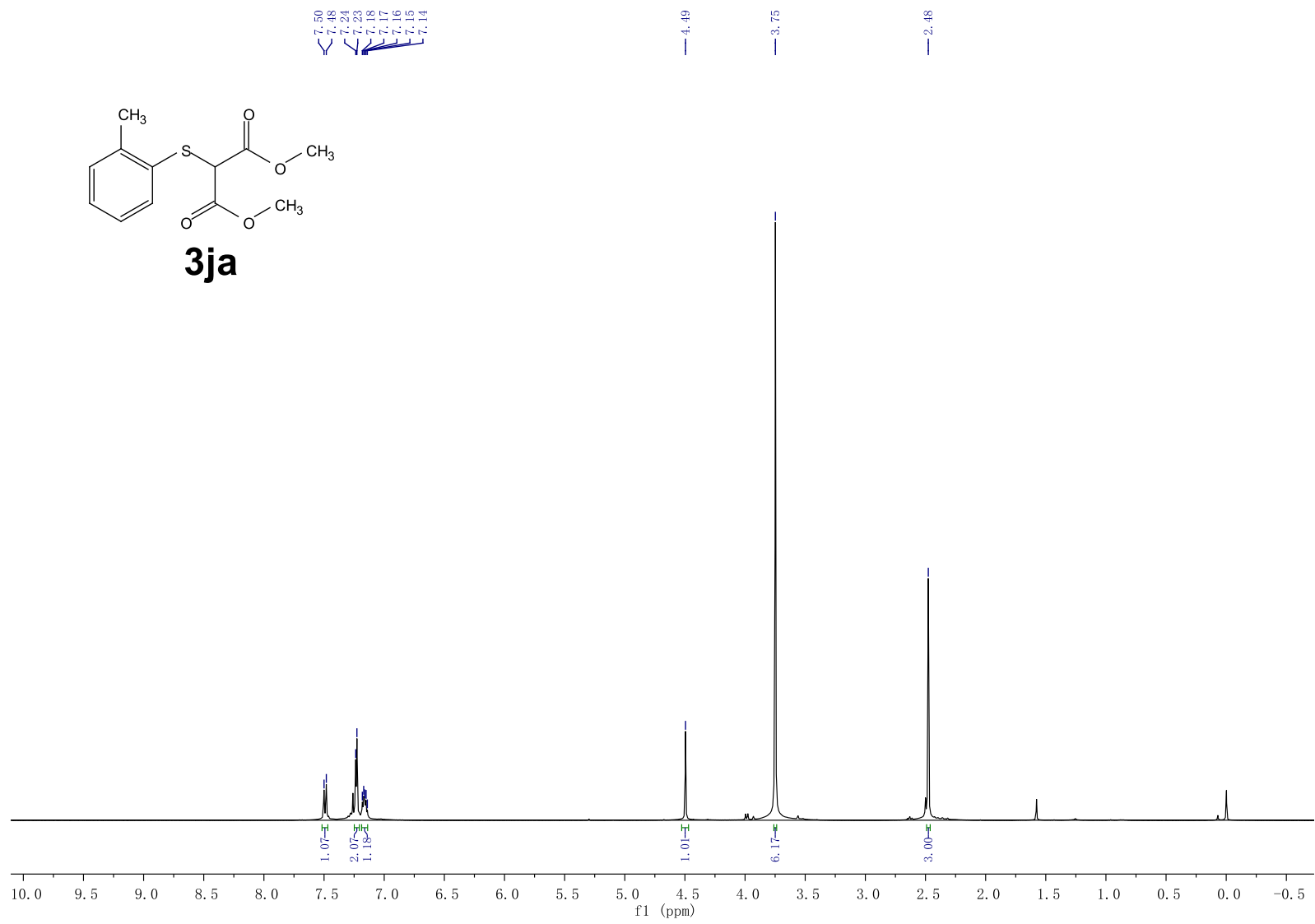


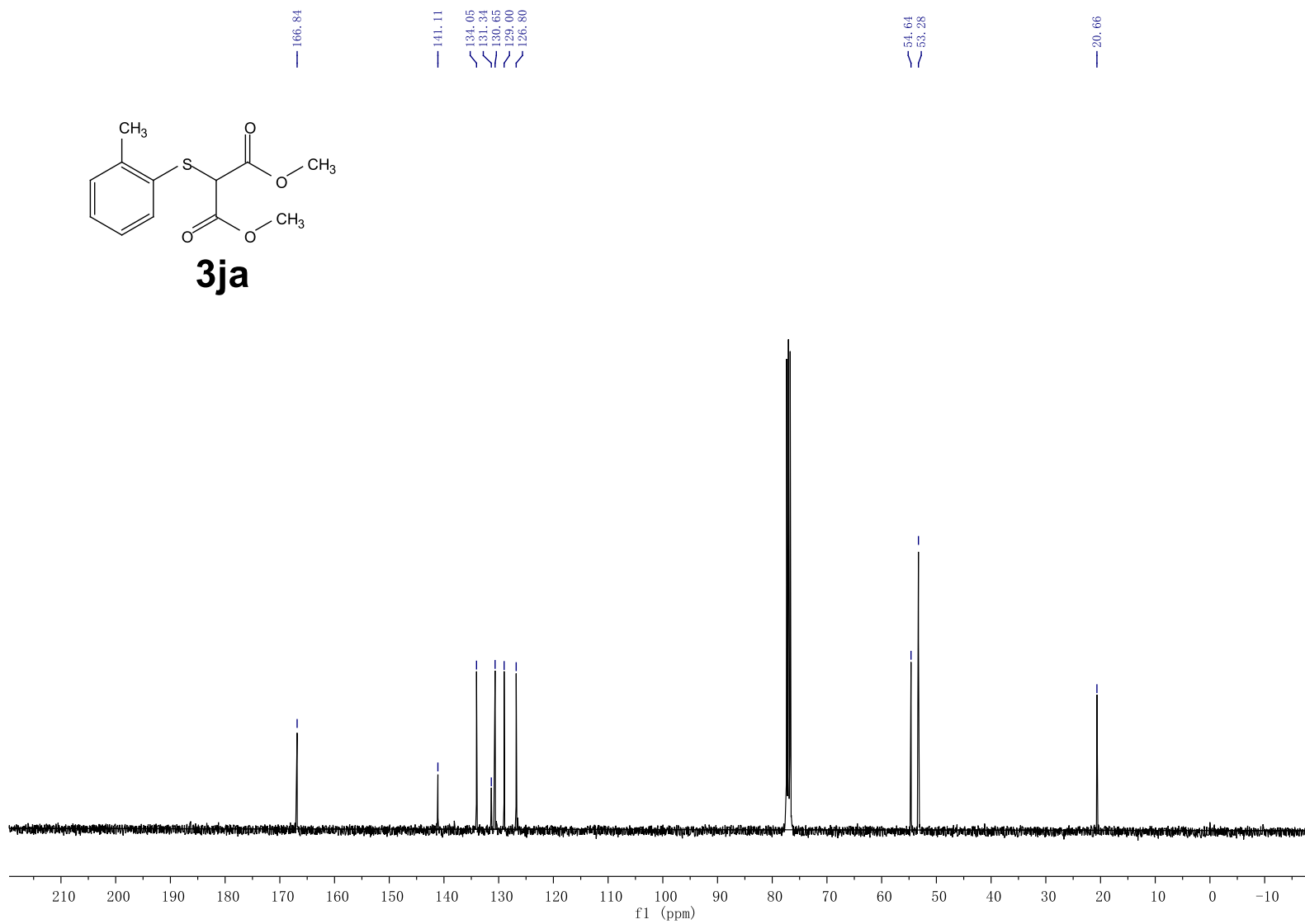
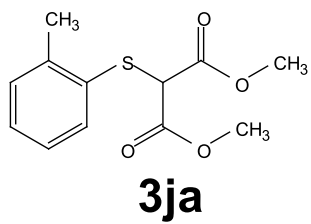


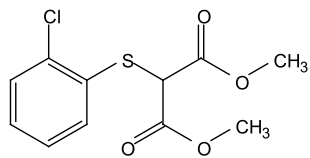




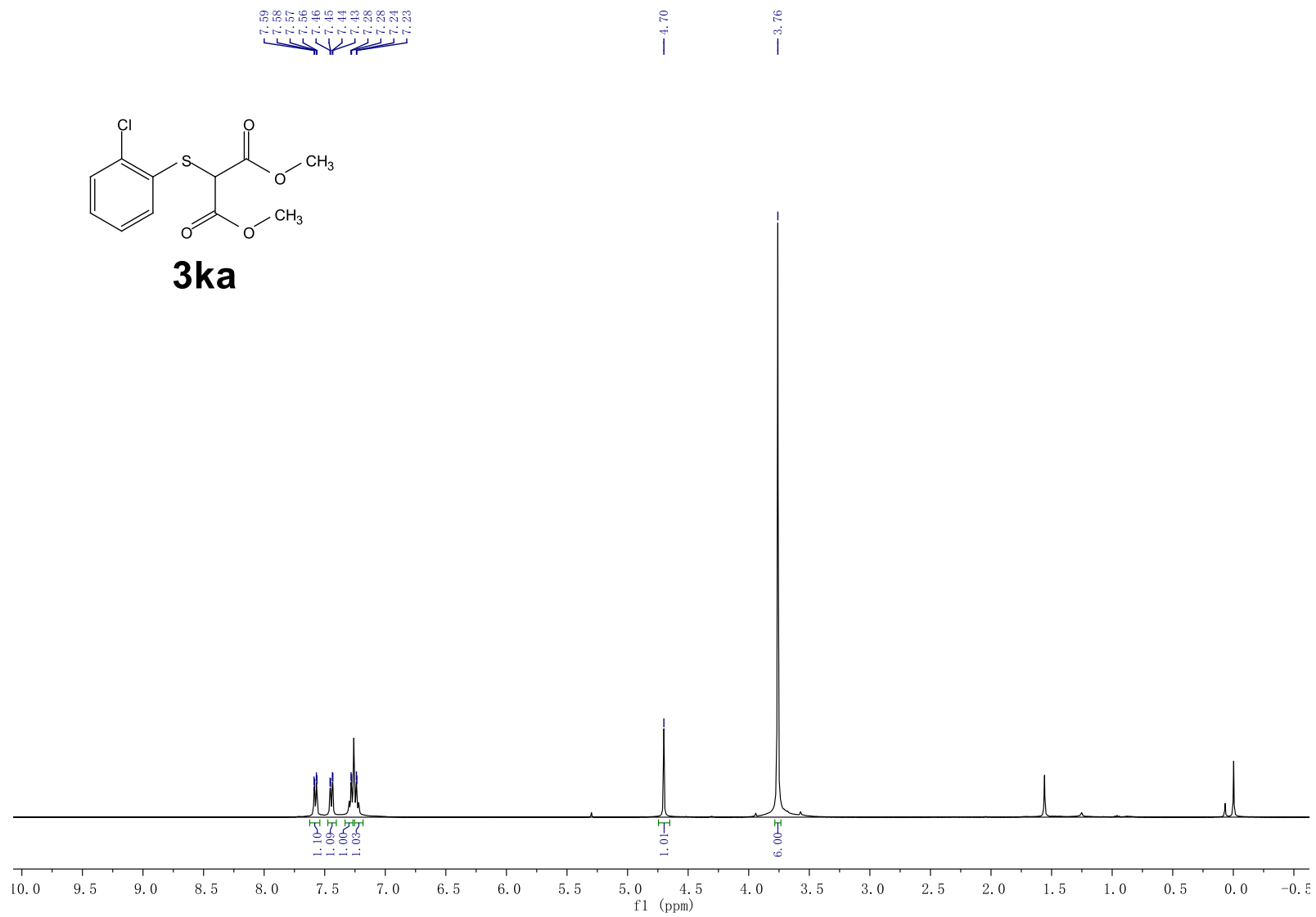
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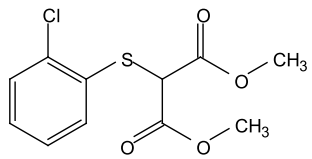




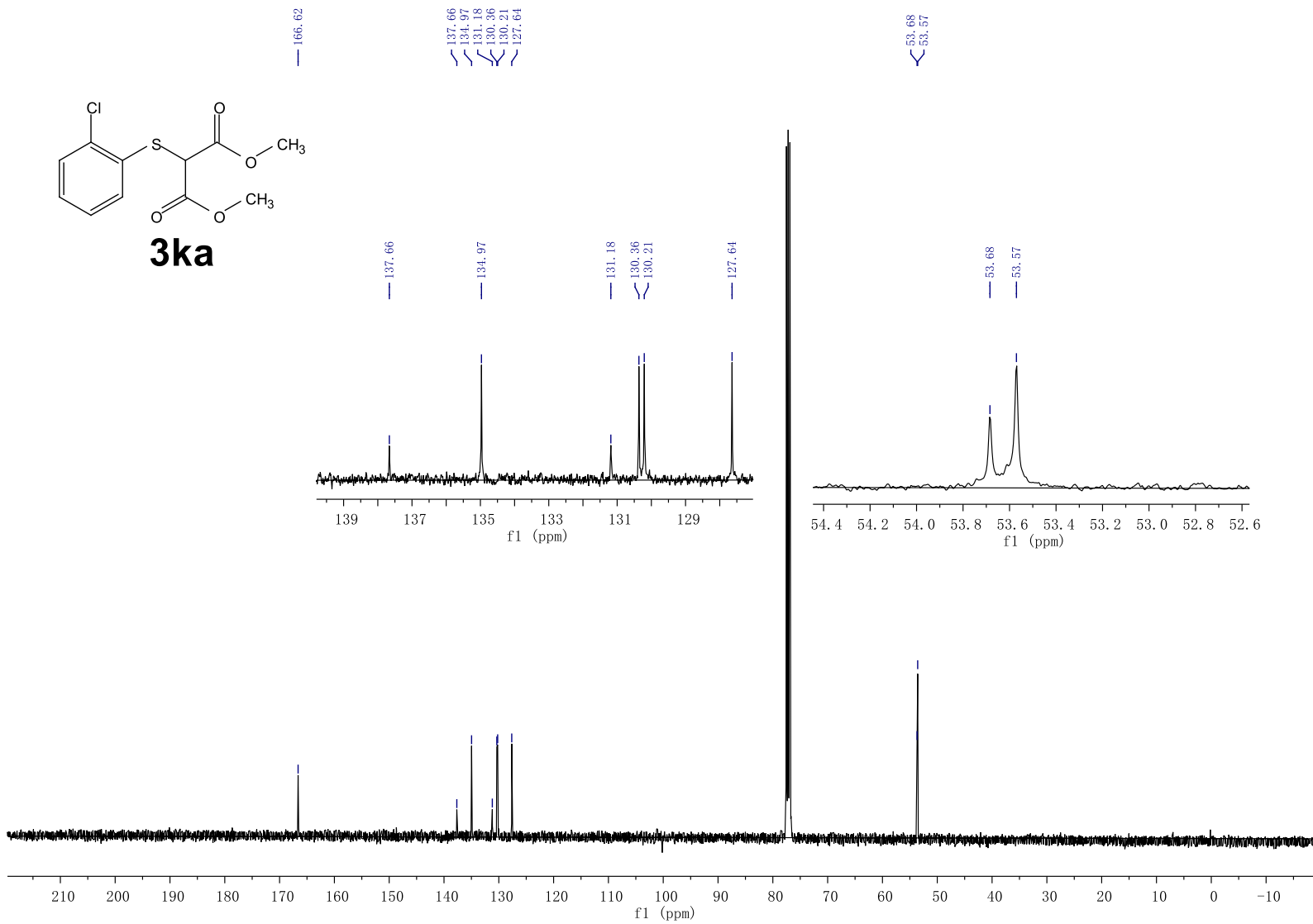


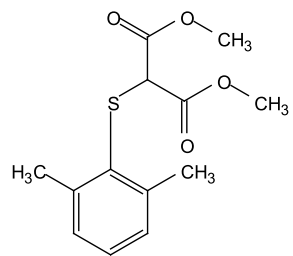
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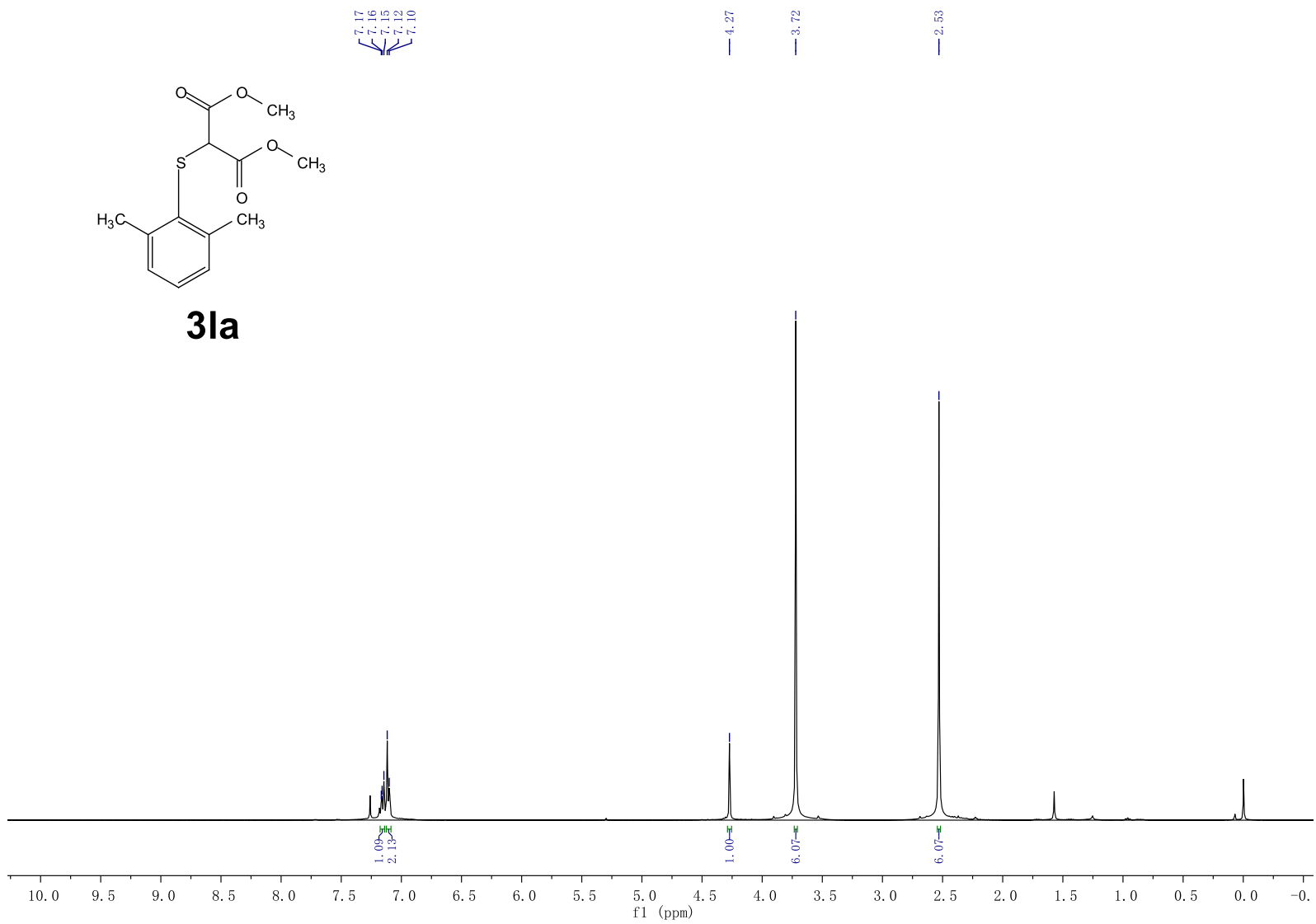


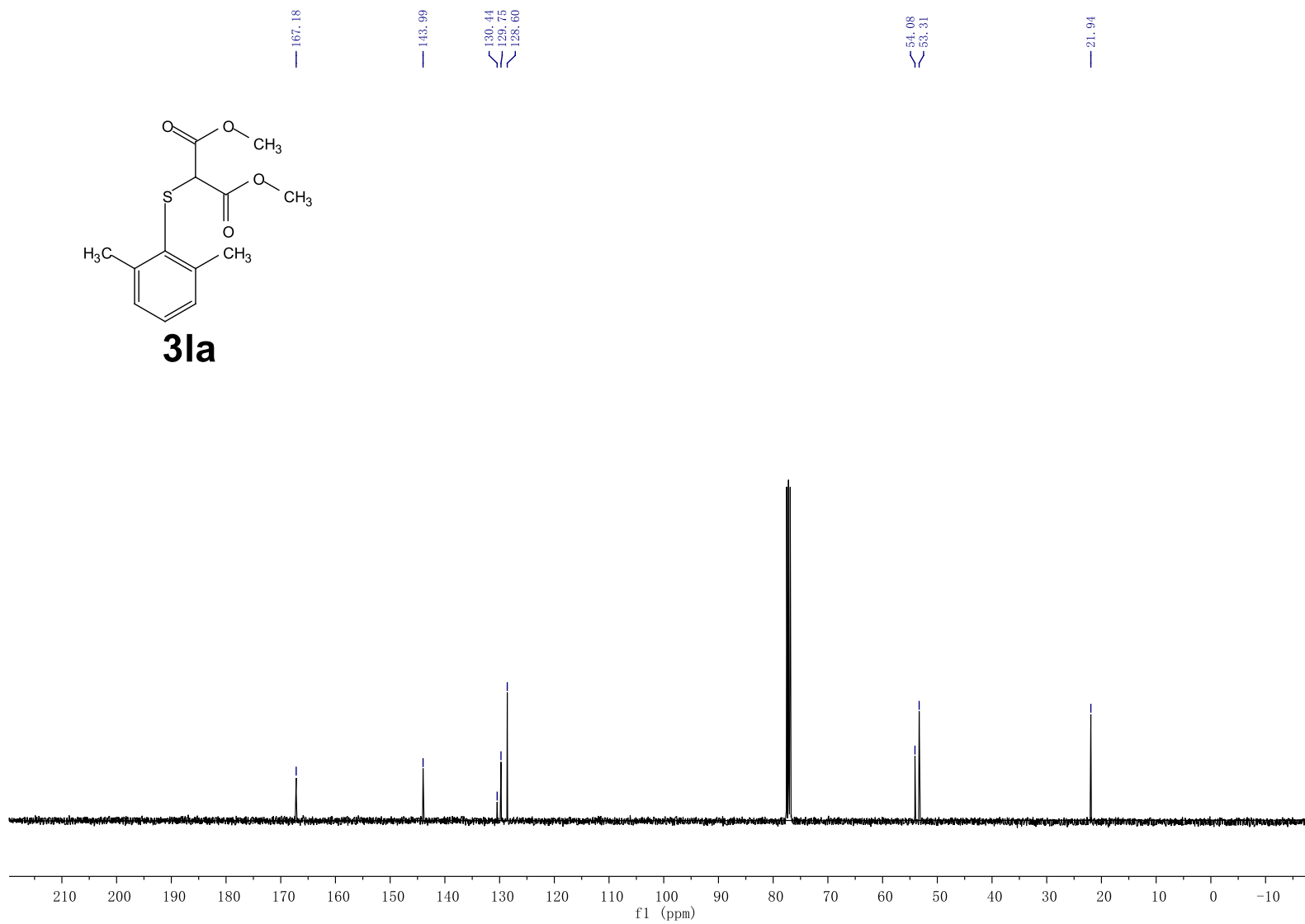
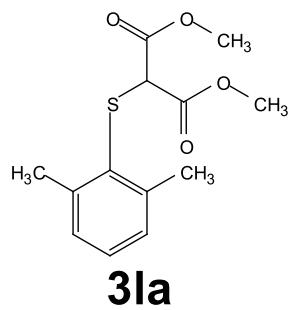
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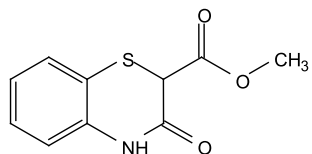




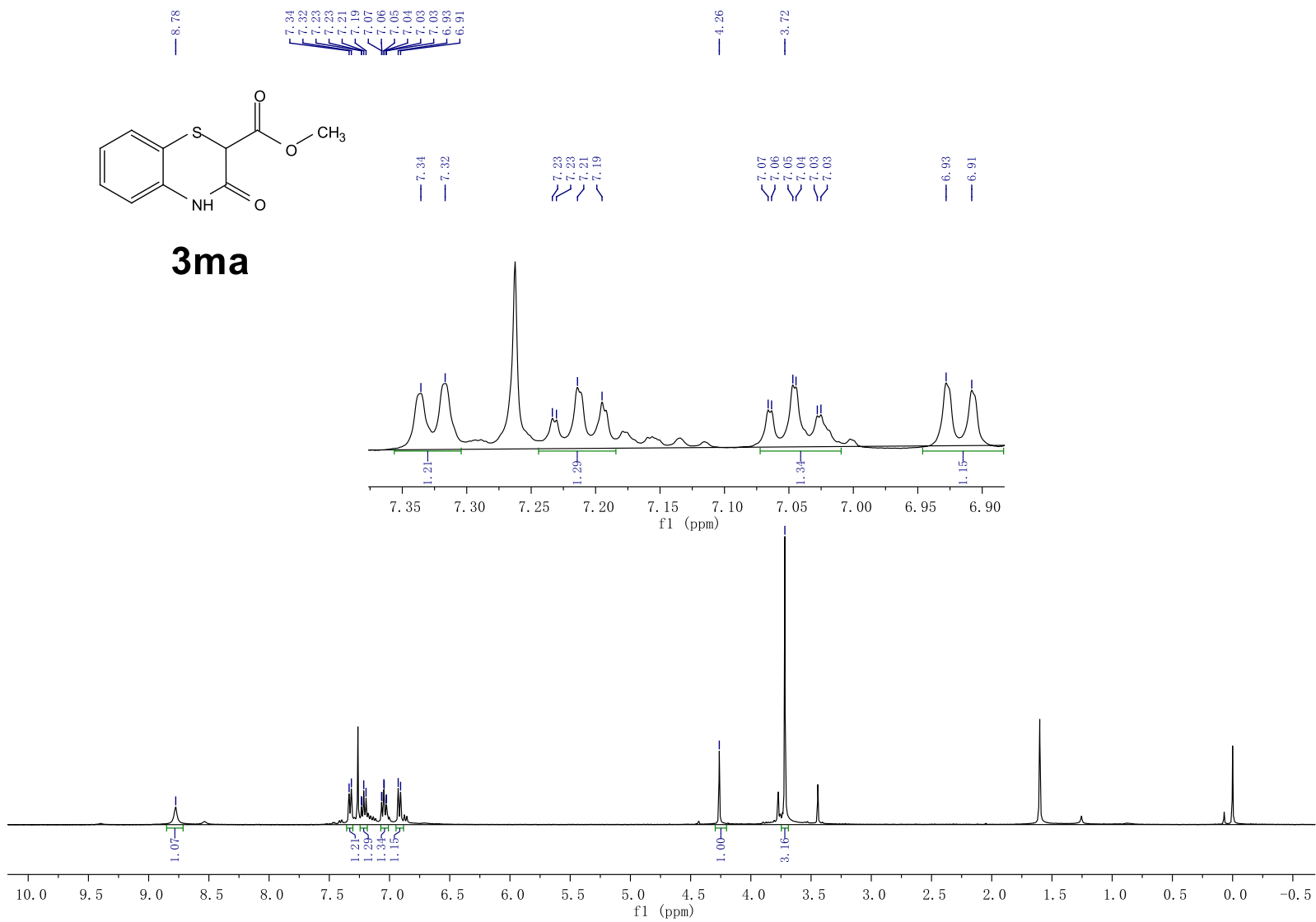
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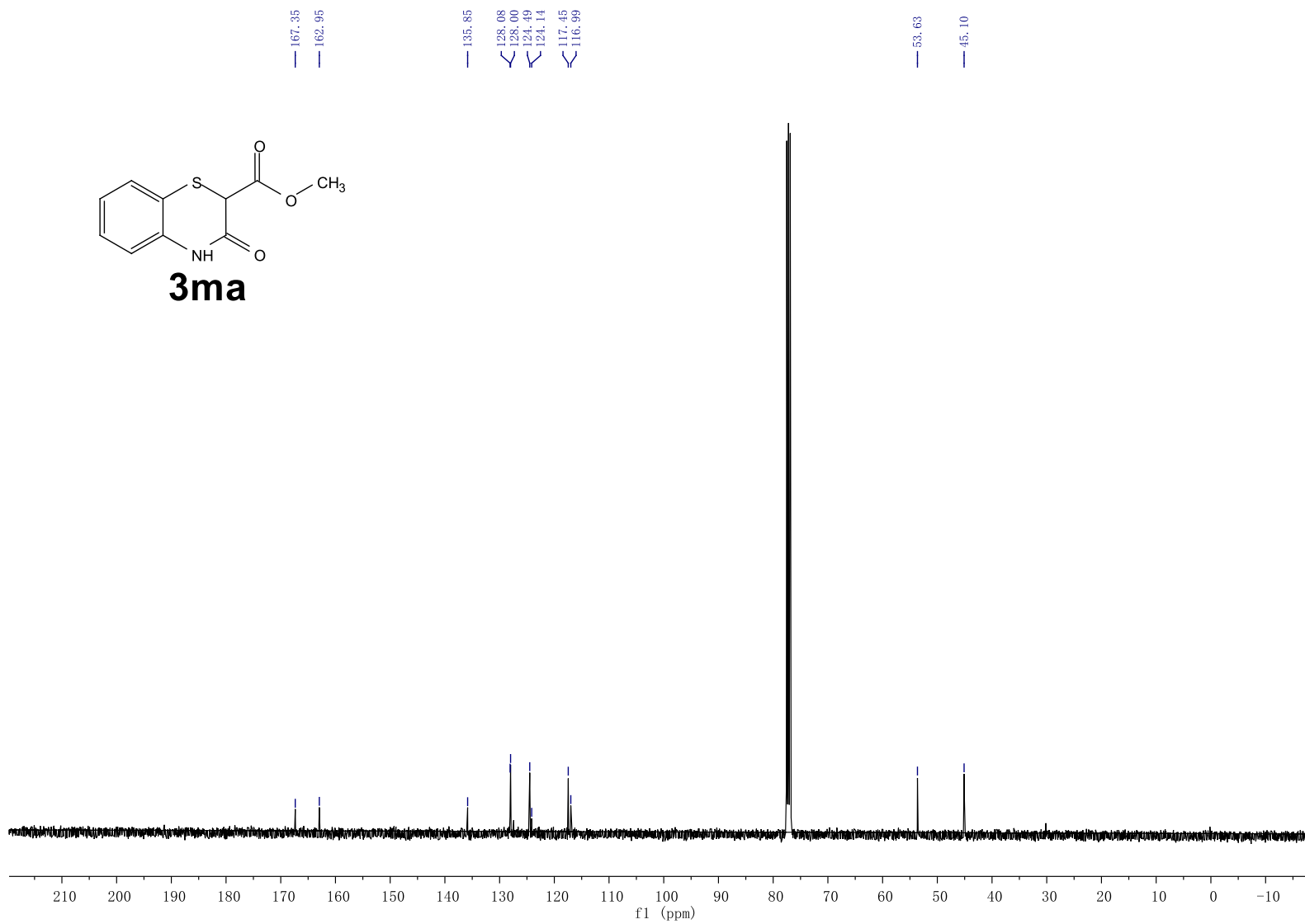
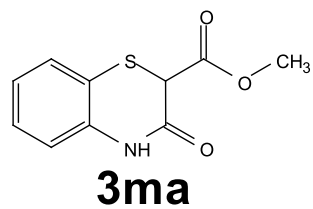


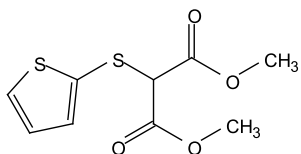


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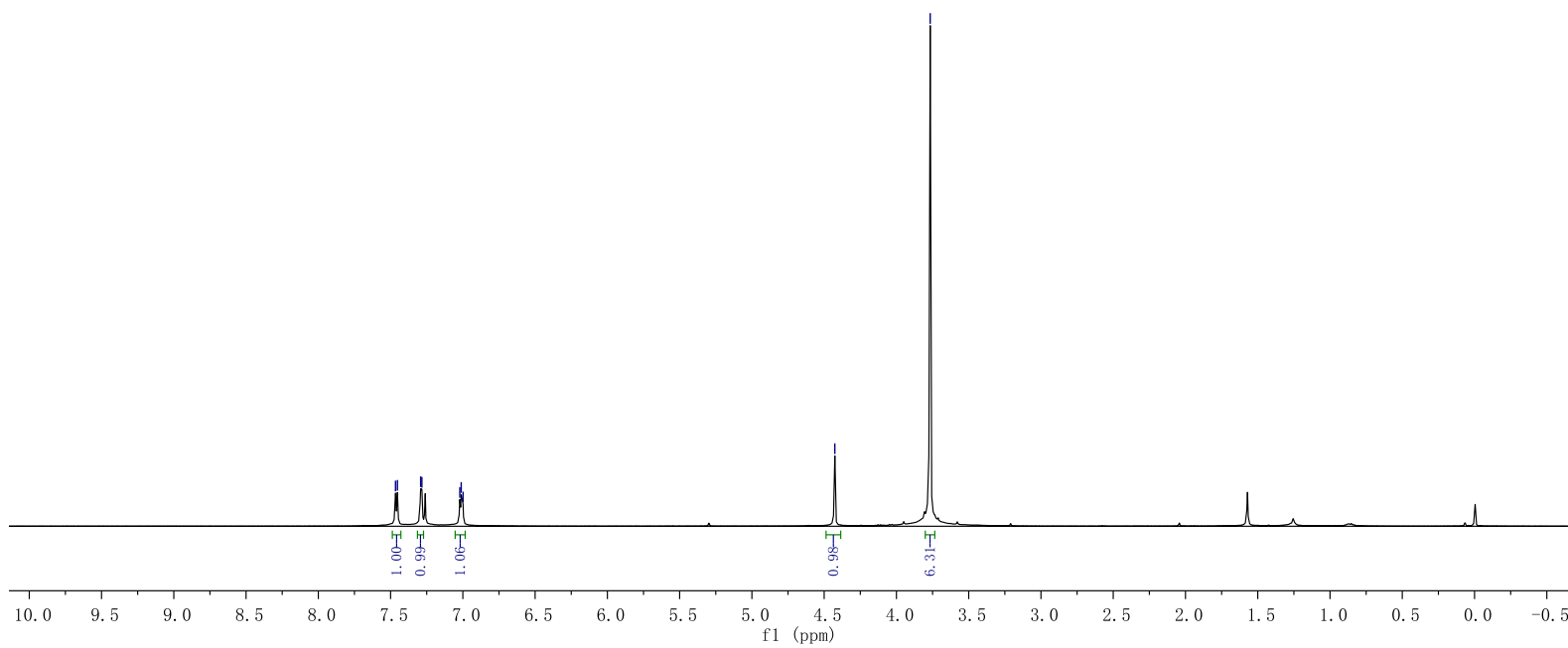


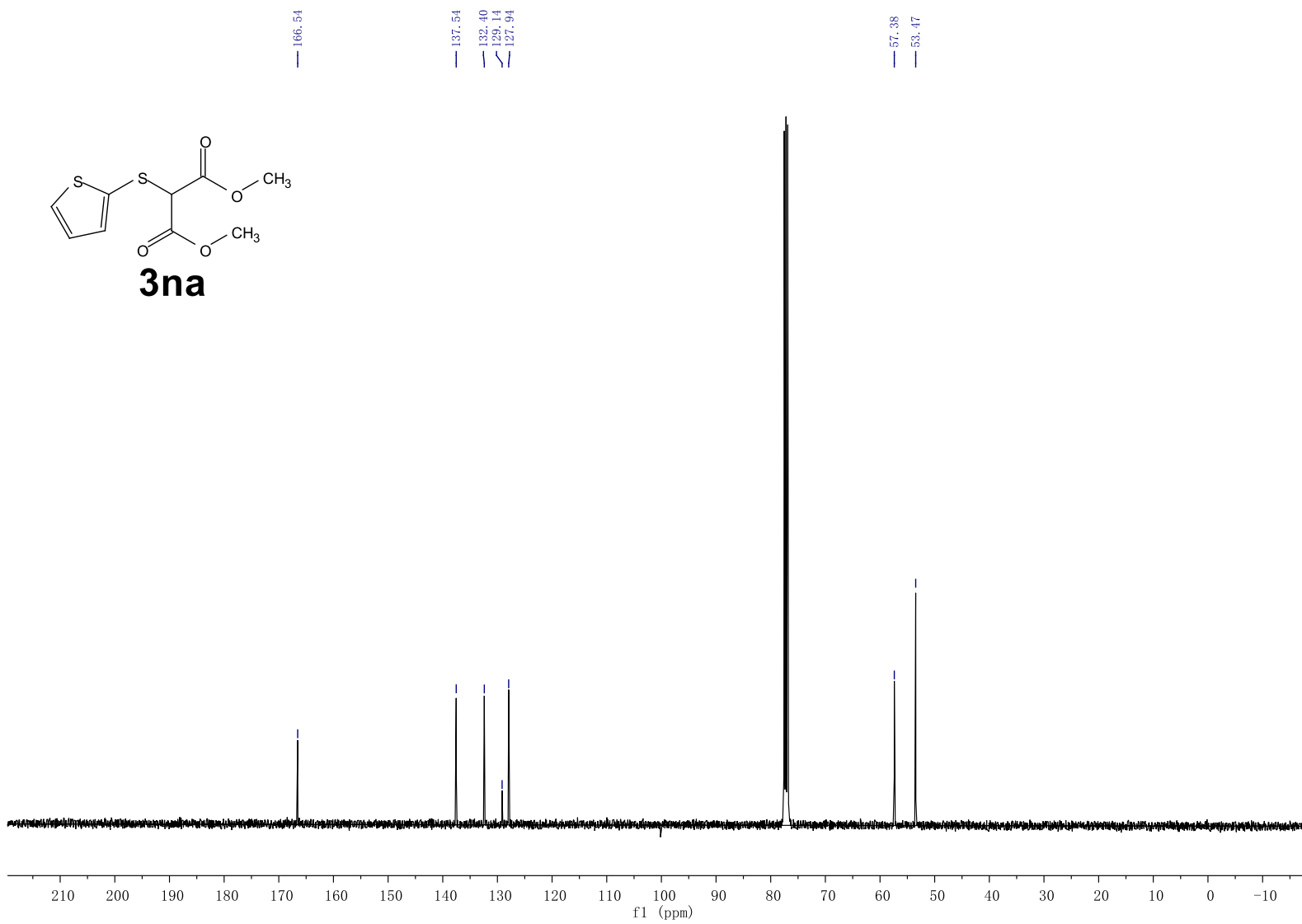
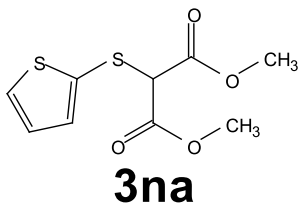
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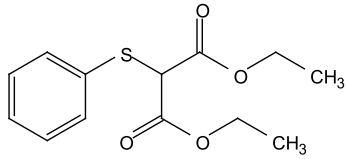
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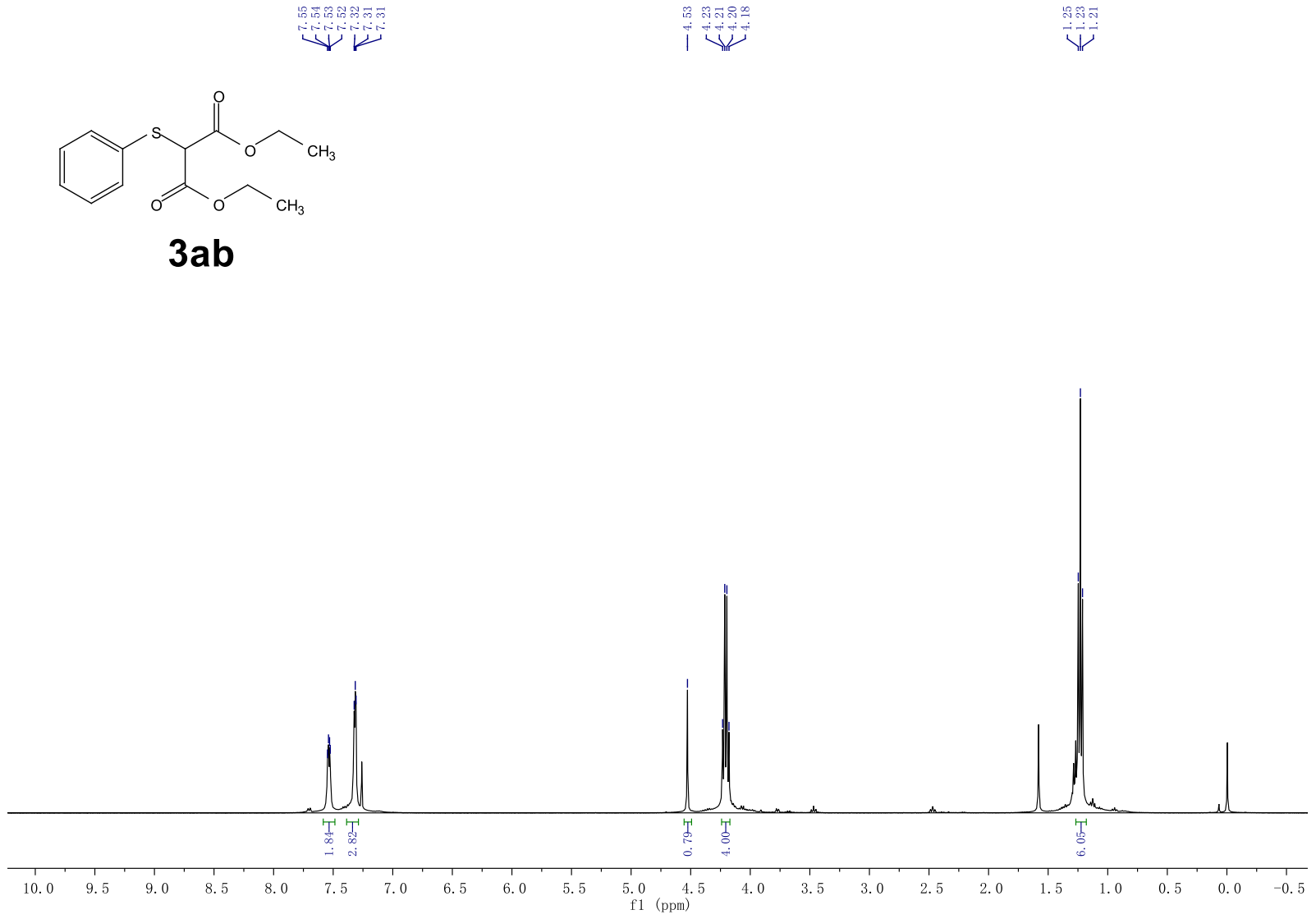
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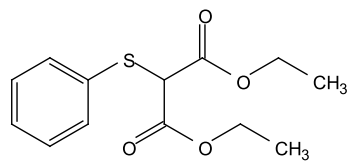




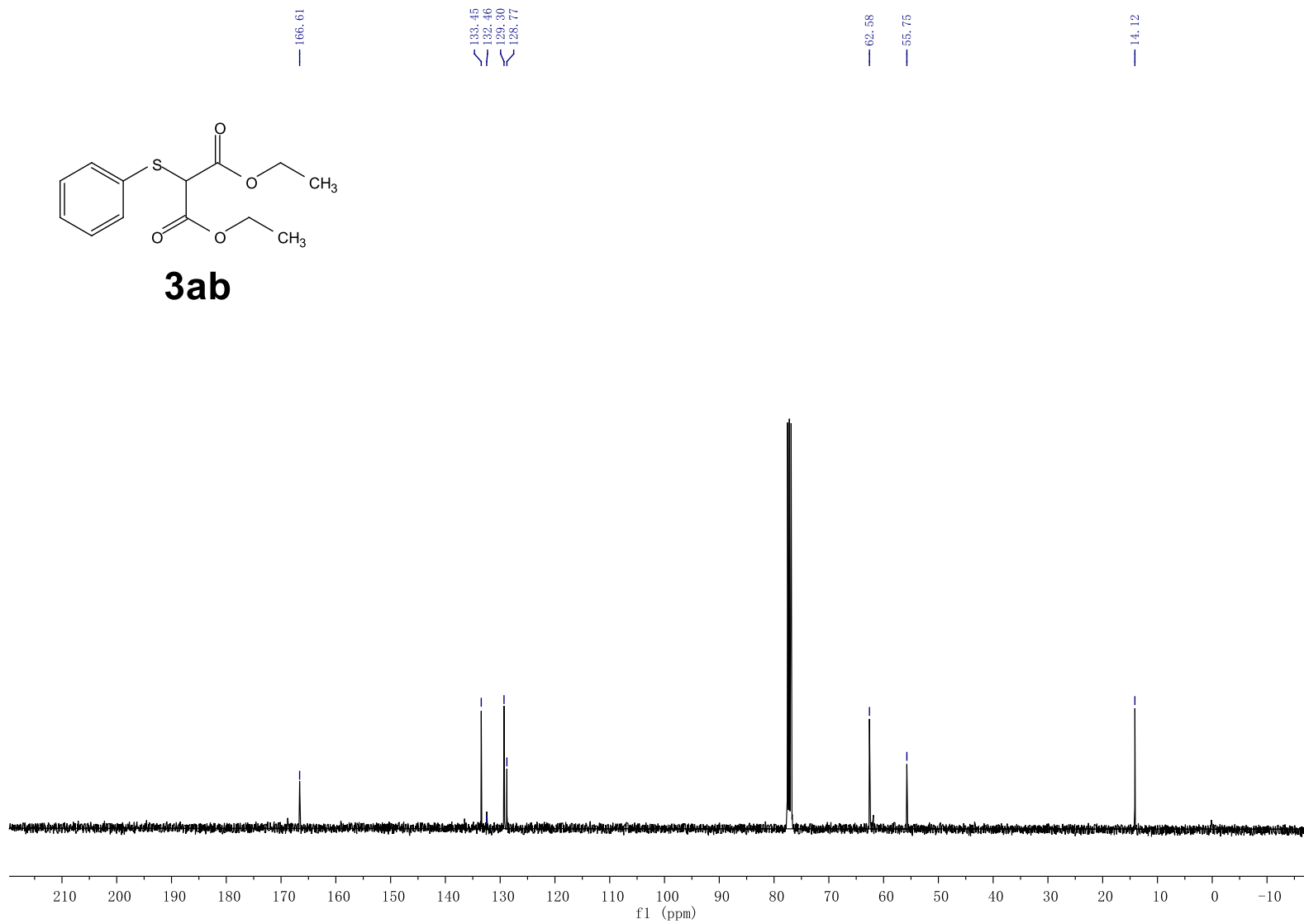


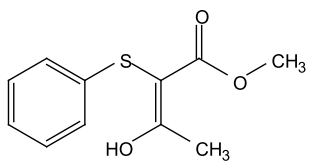
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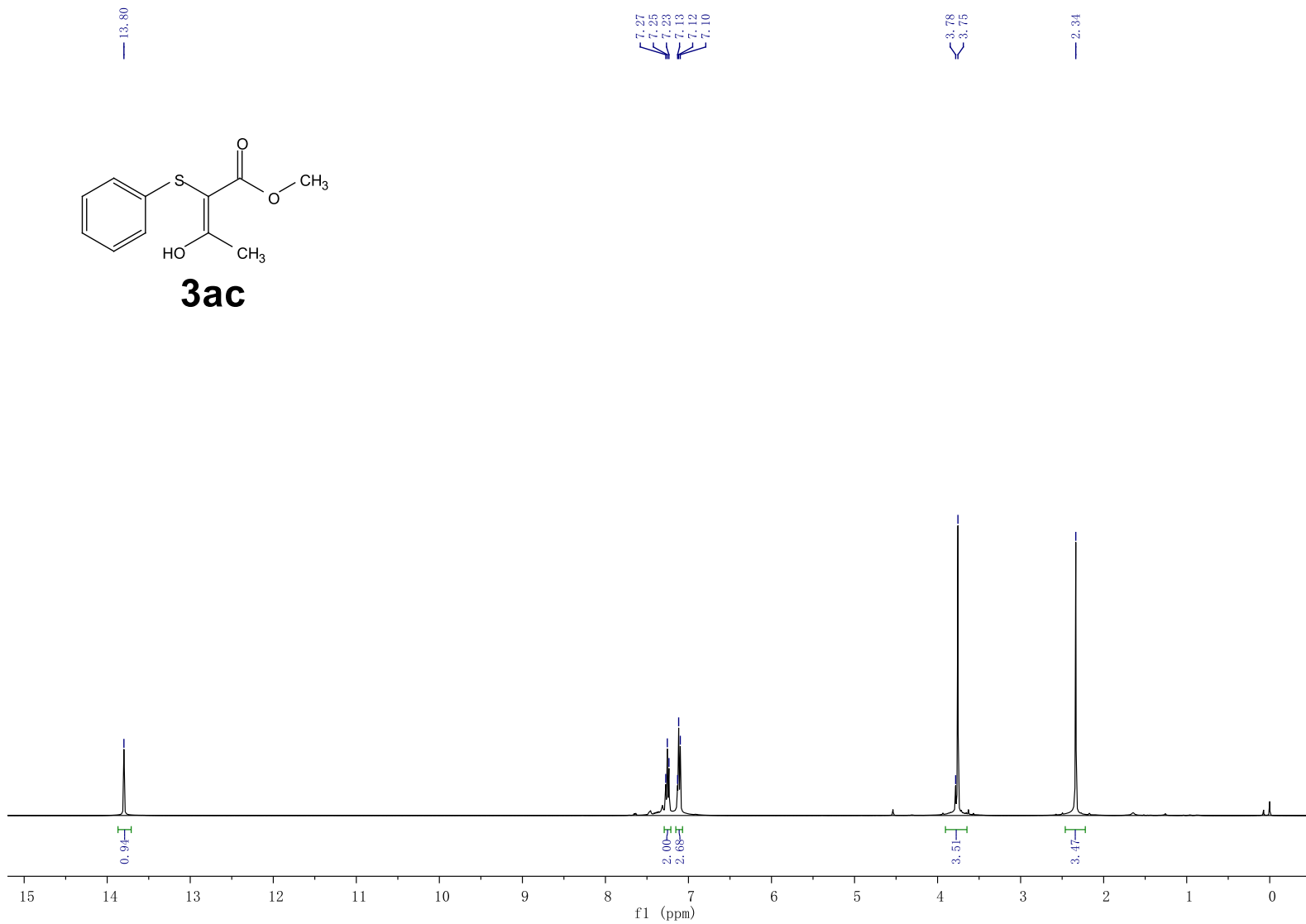


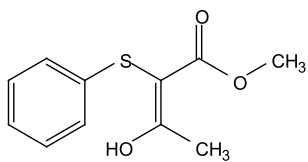
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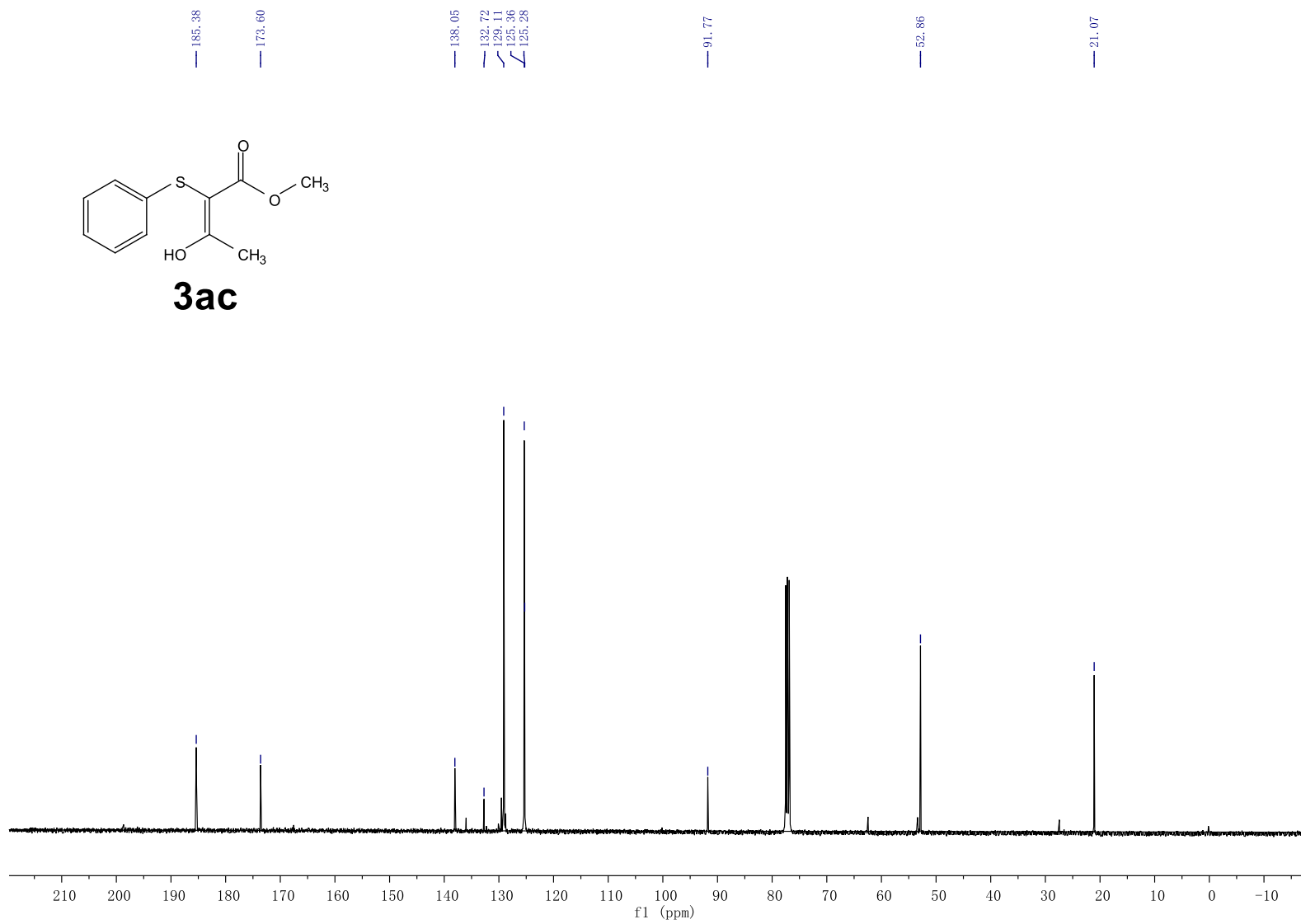


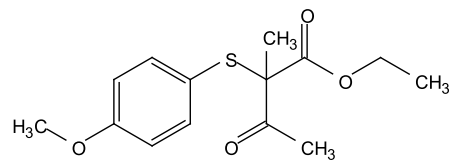
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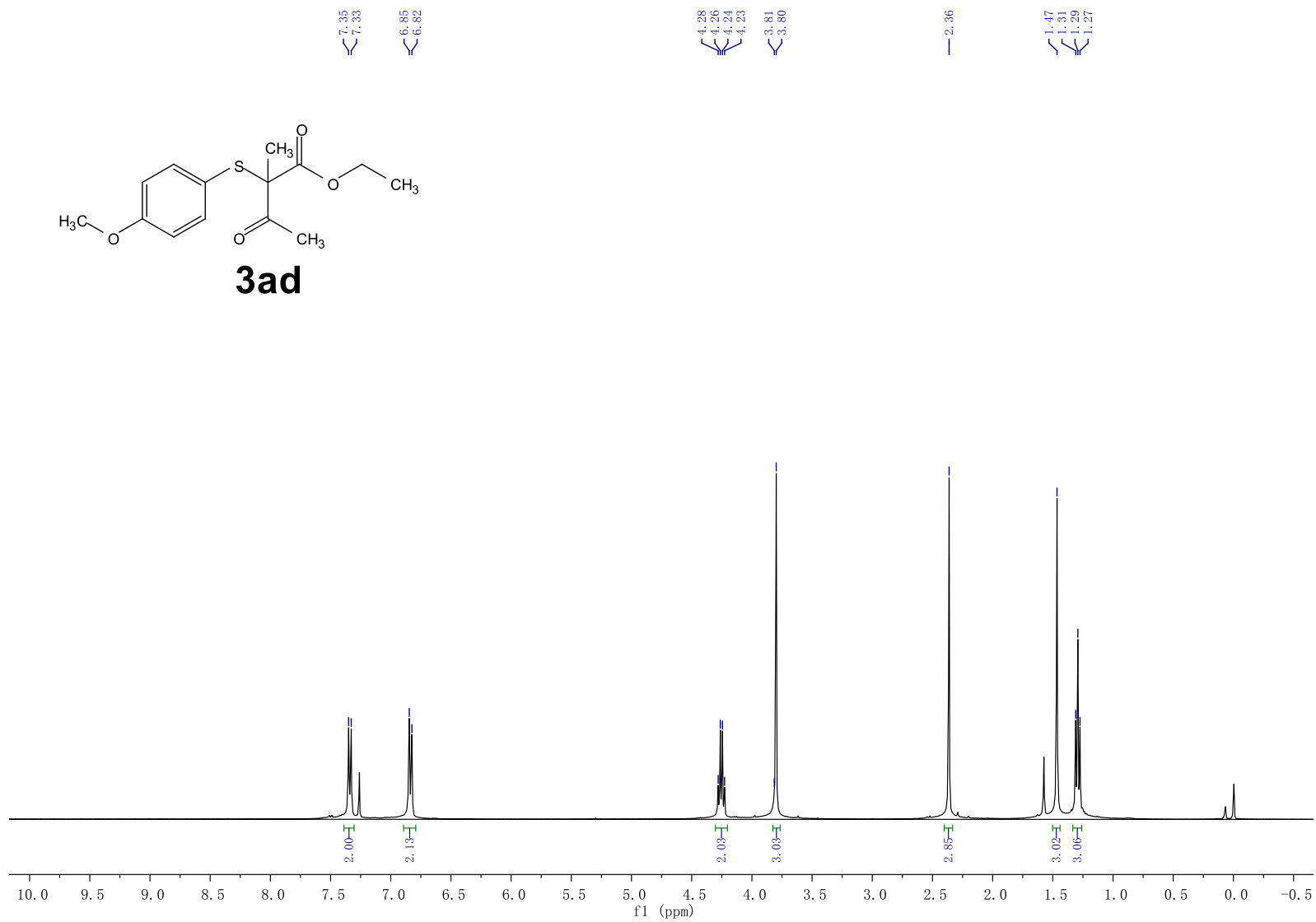


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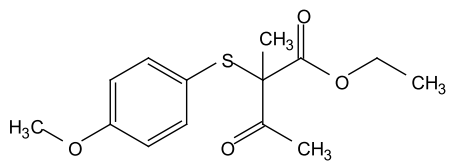




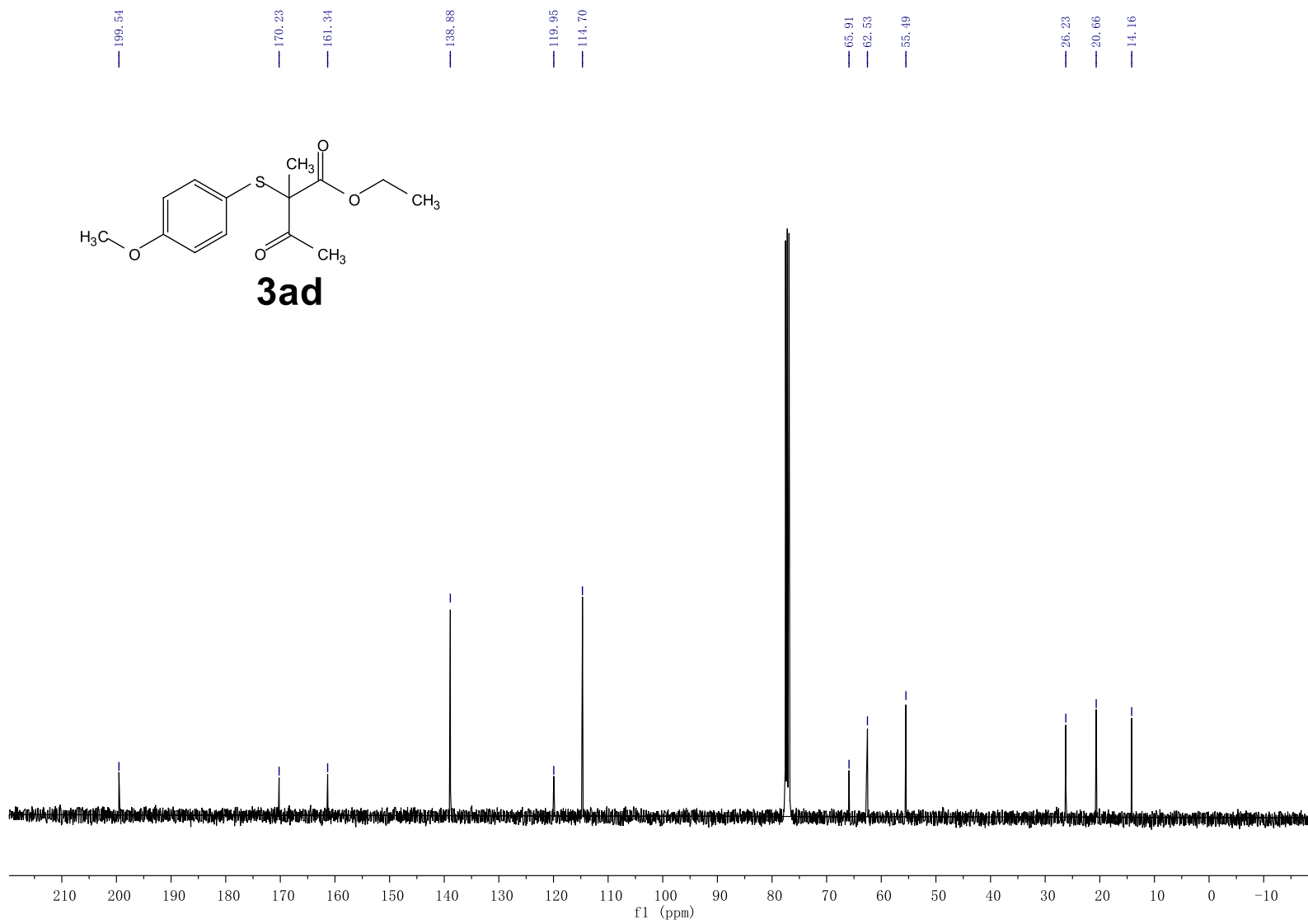
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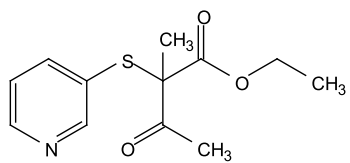




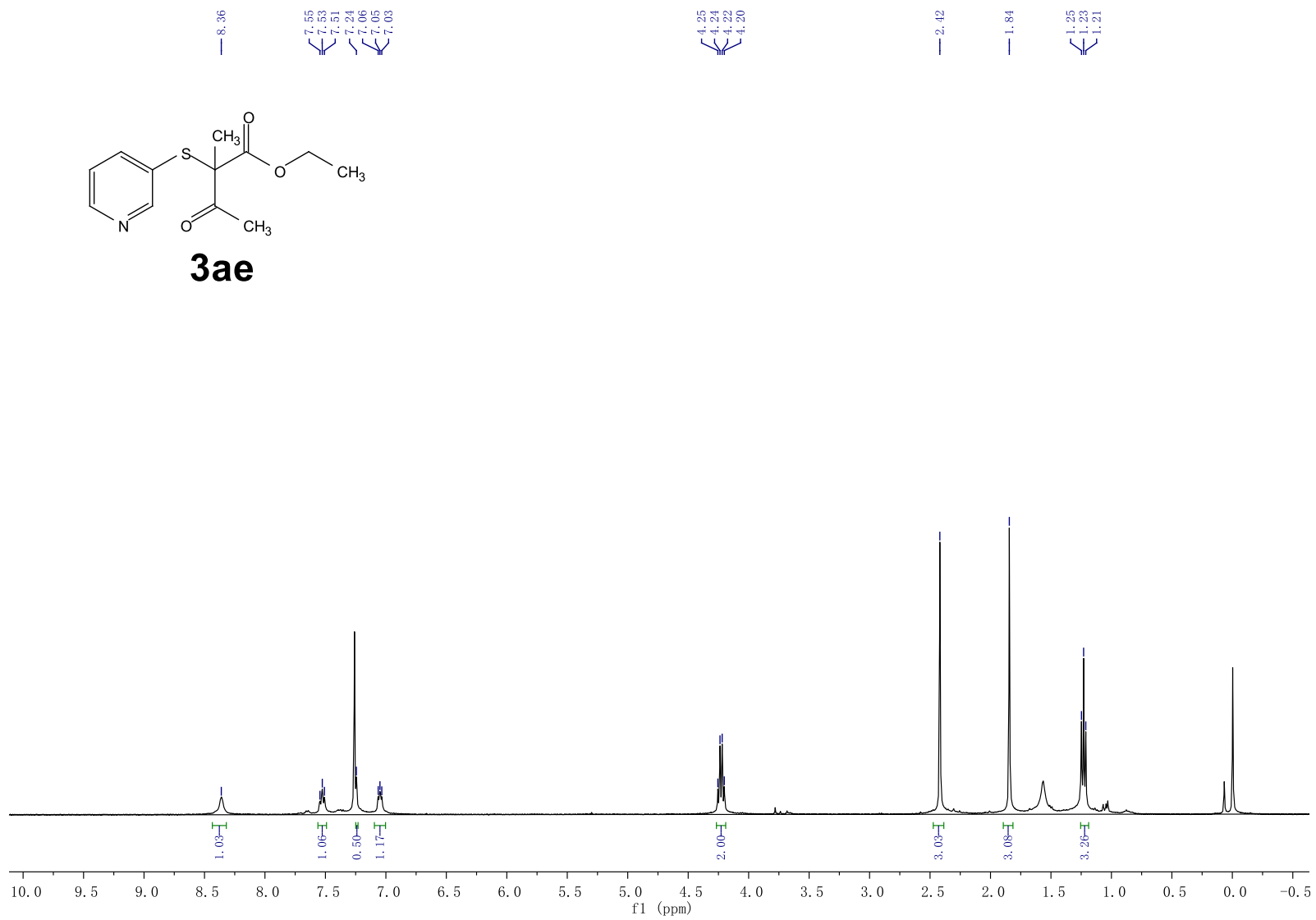


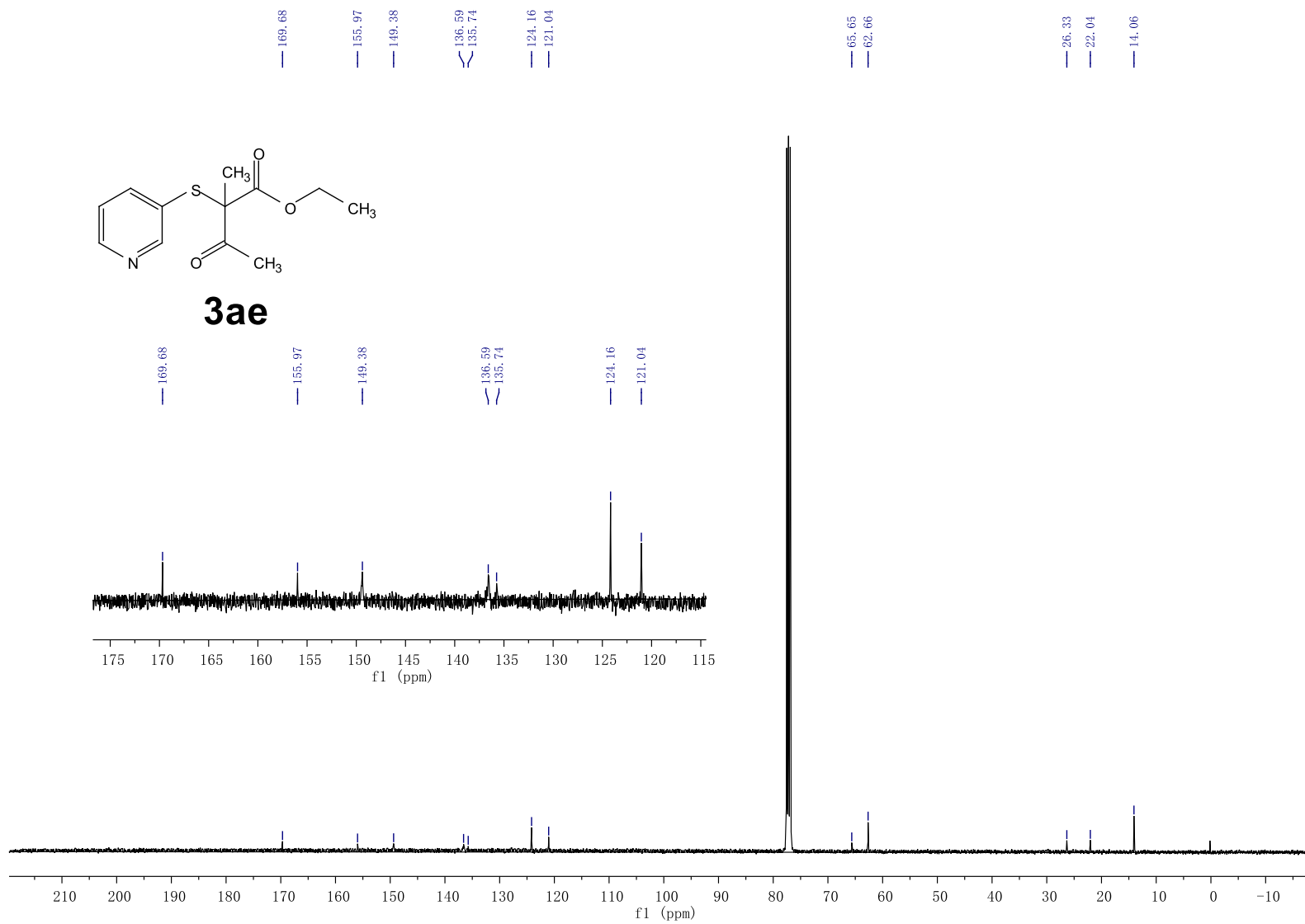
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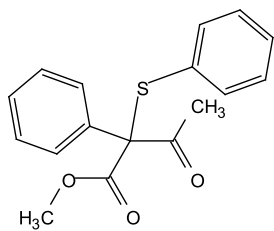




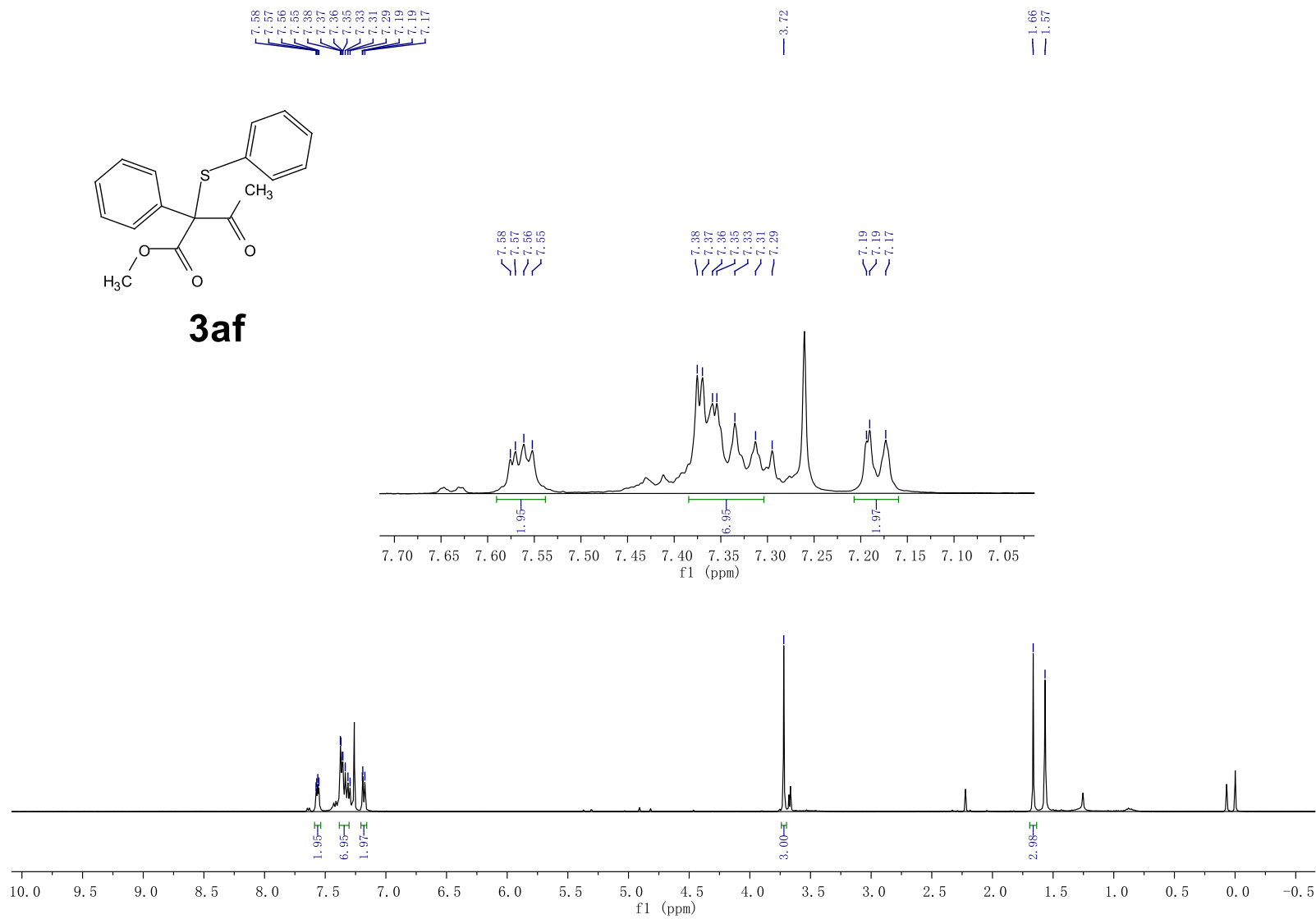
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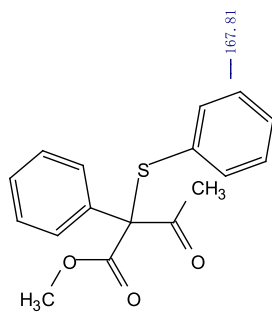




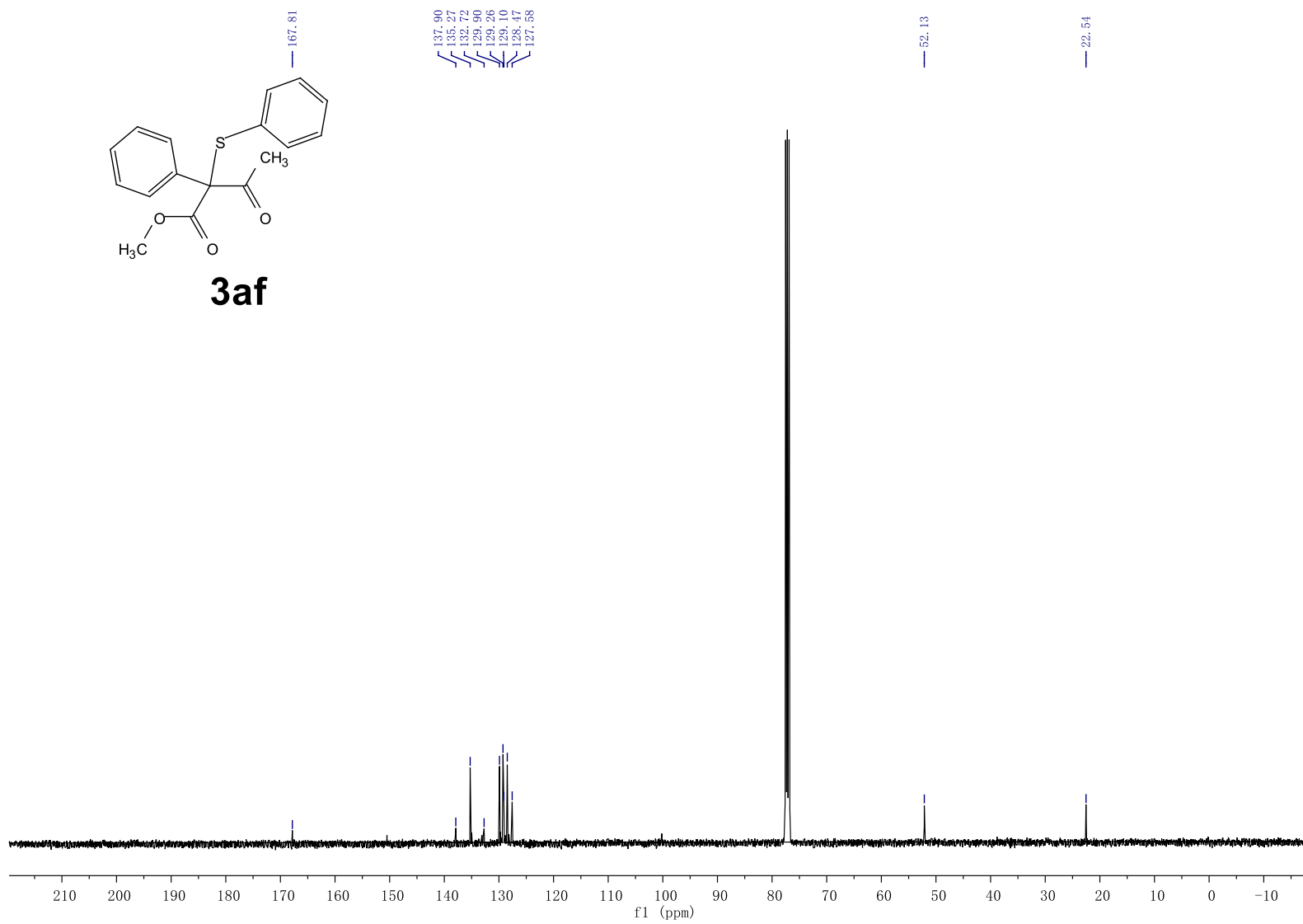


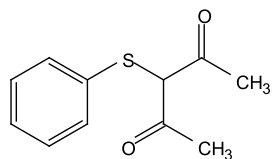
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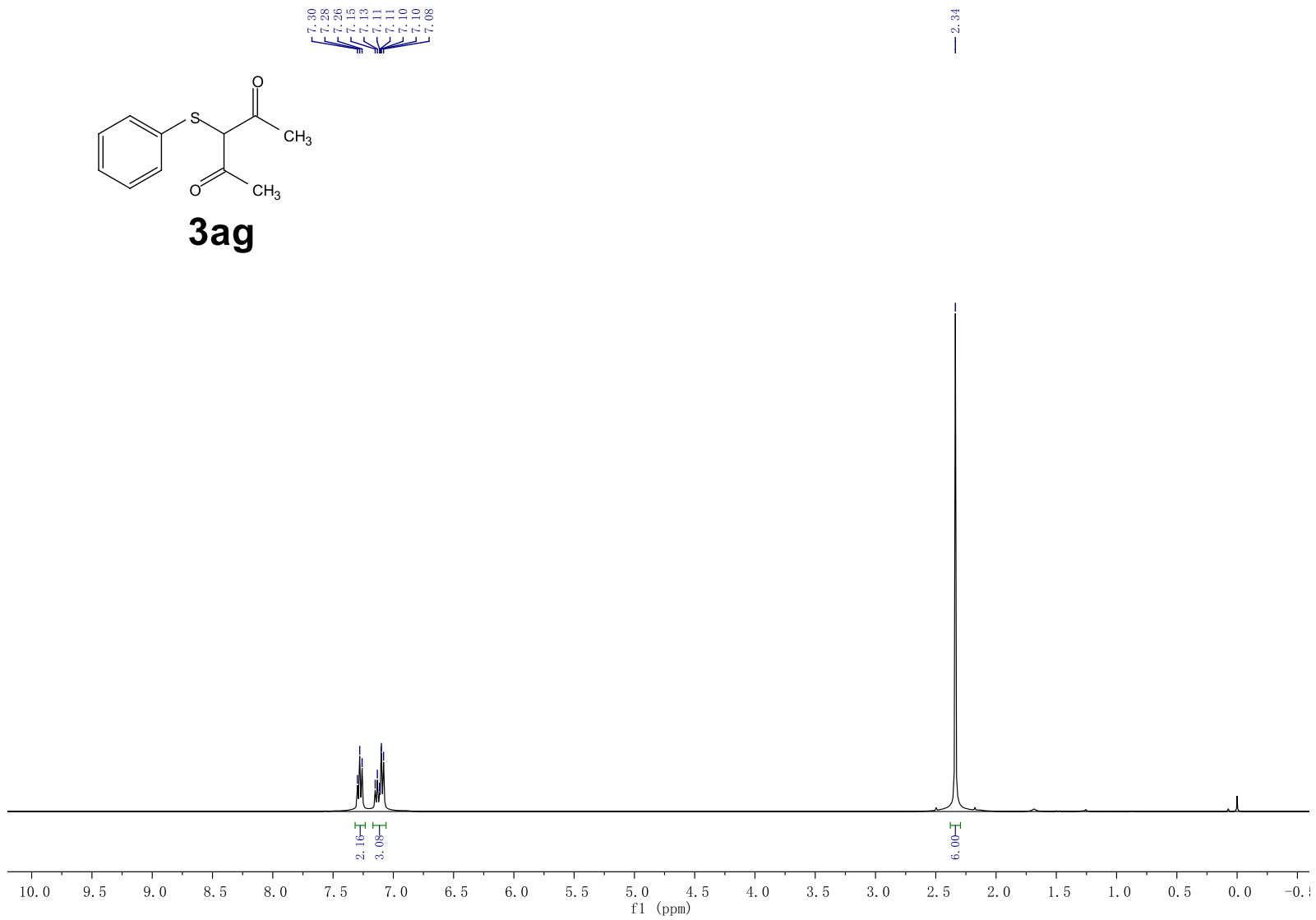
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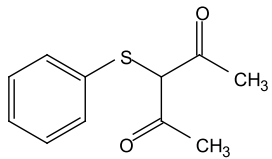




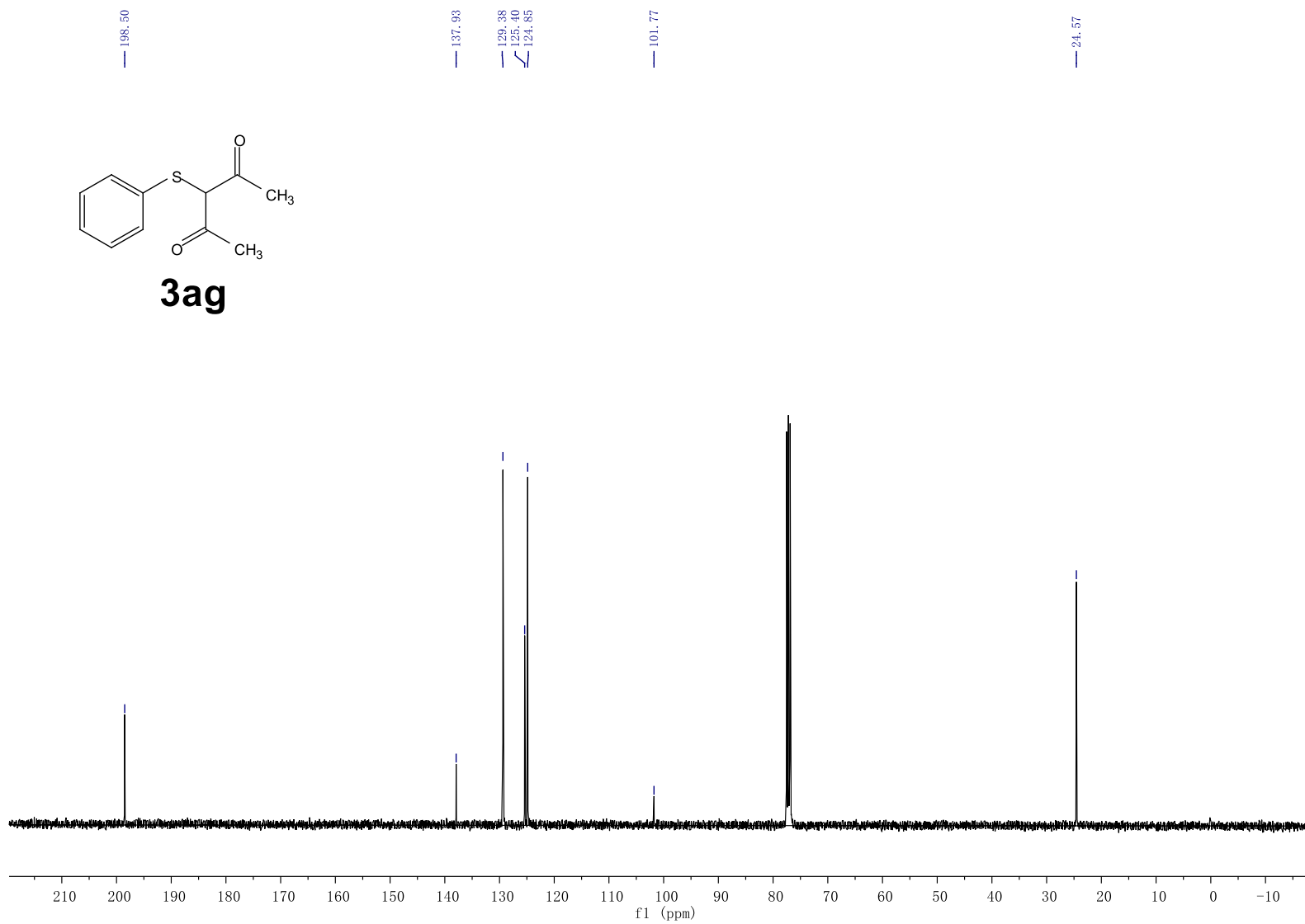
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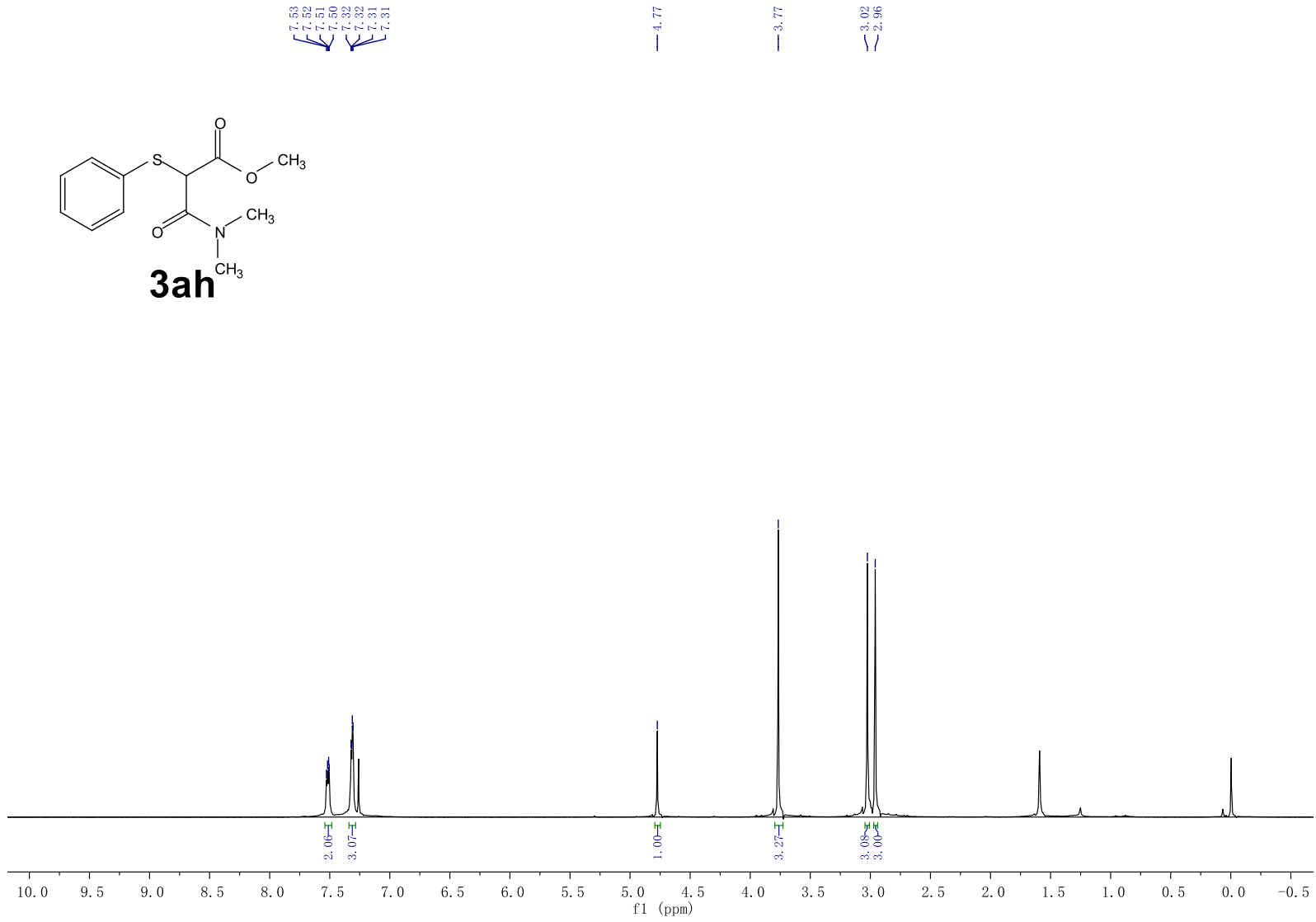
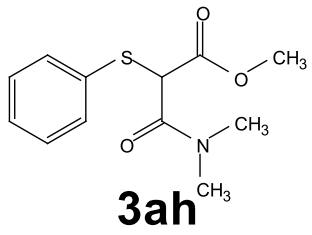
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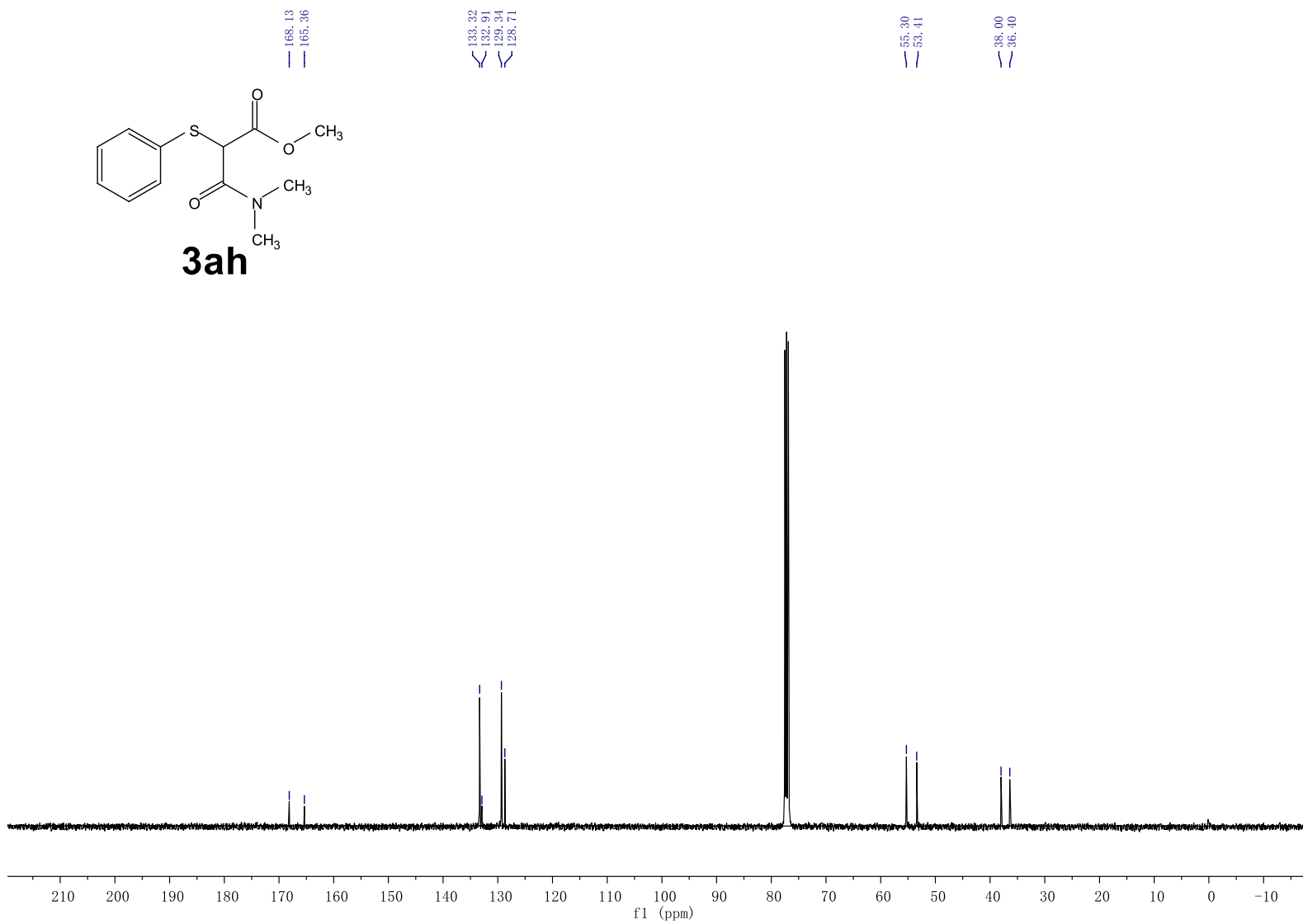
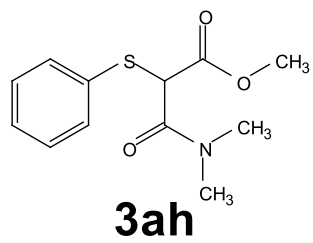


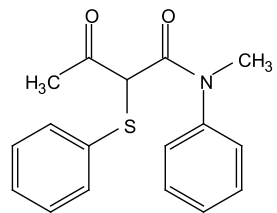
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**3ai**

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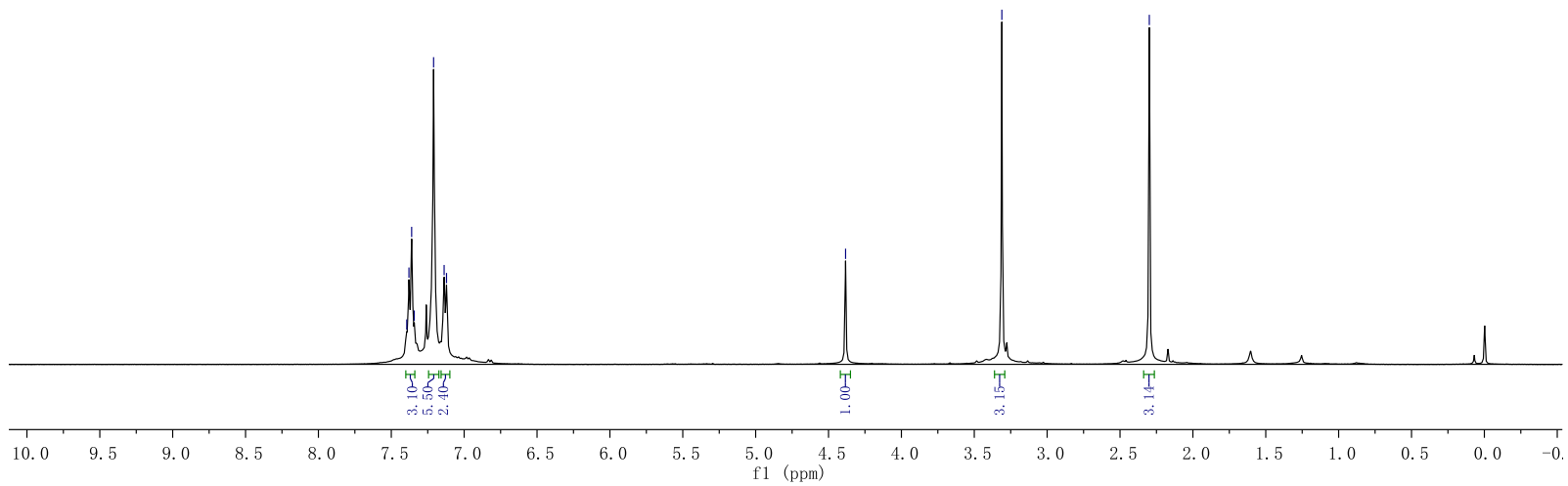
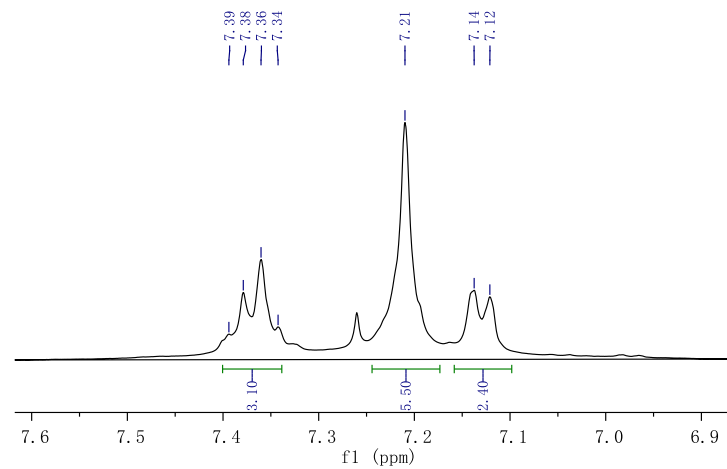
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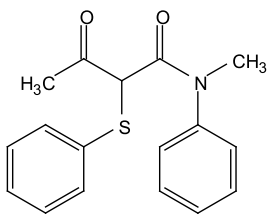
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4.38

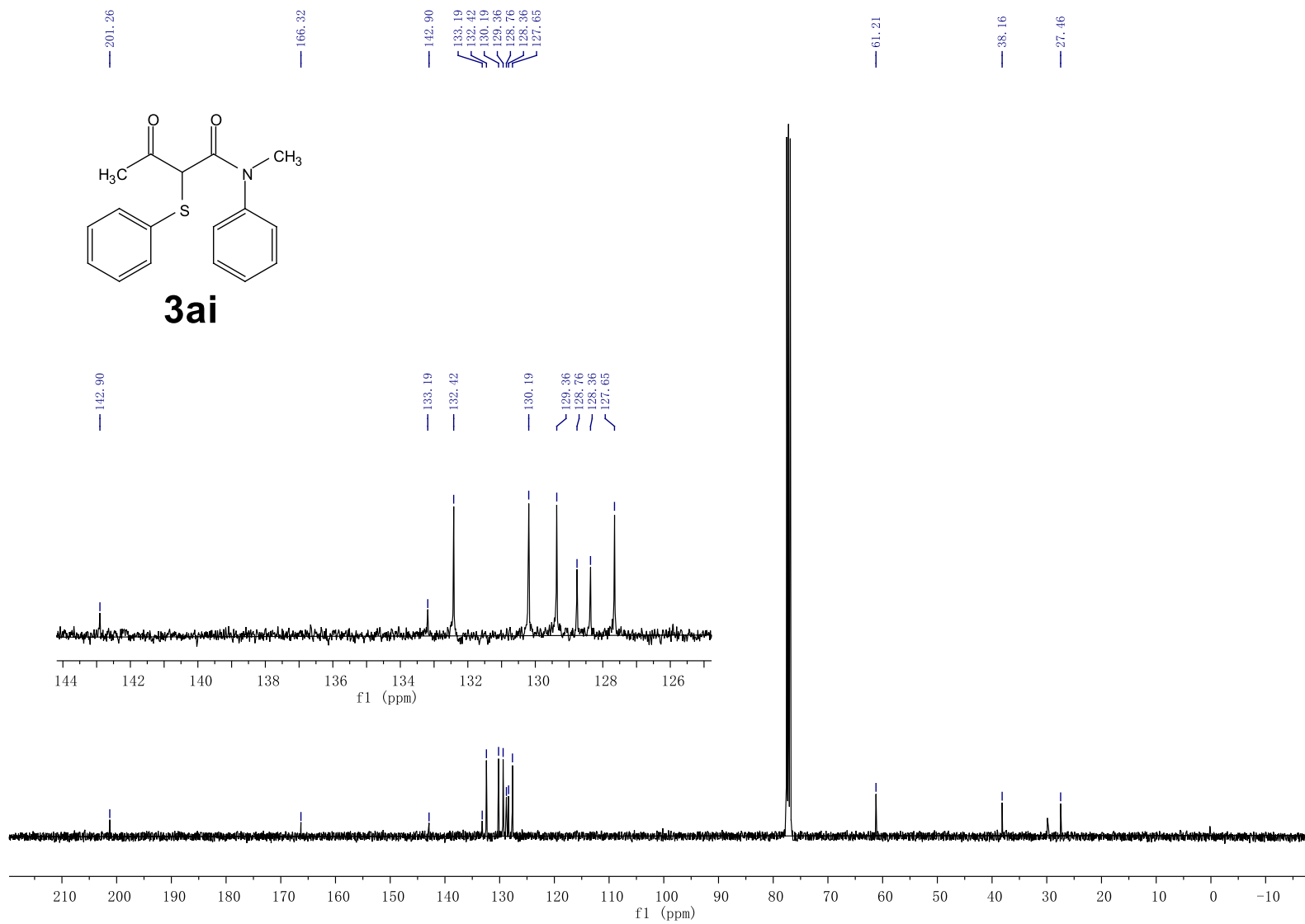
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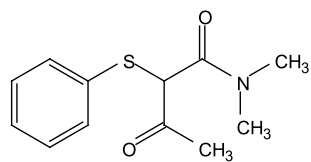
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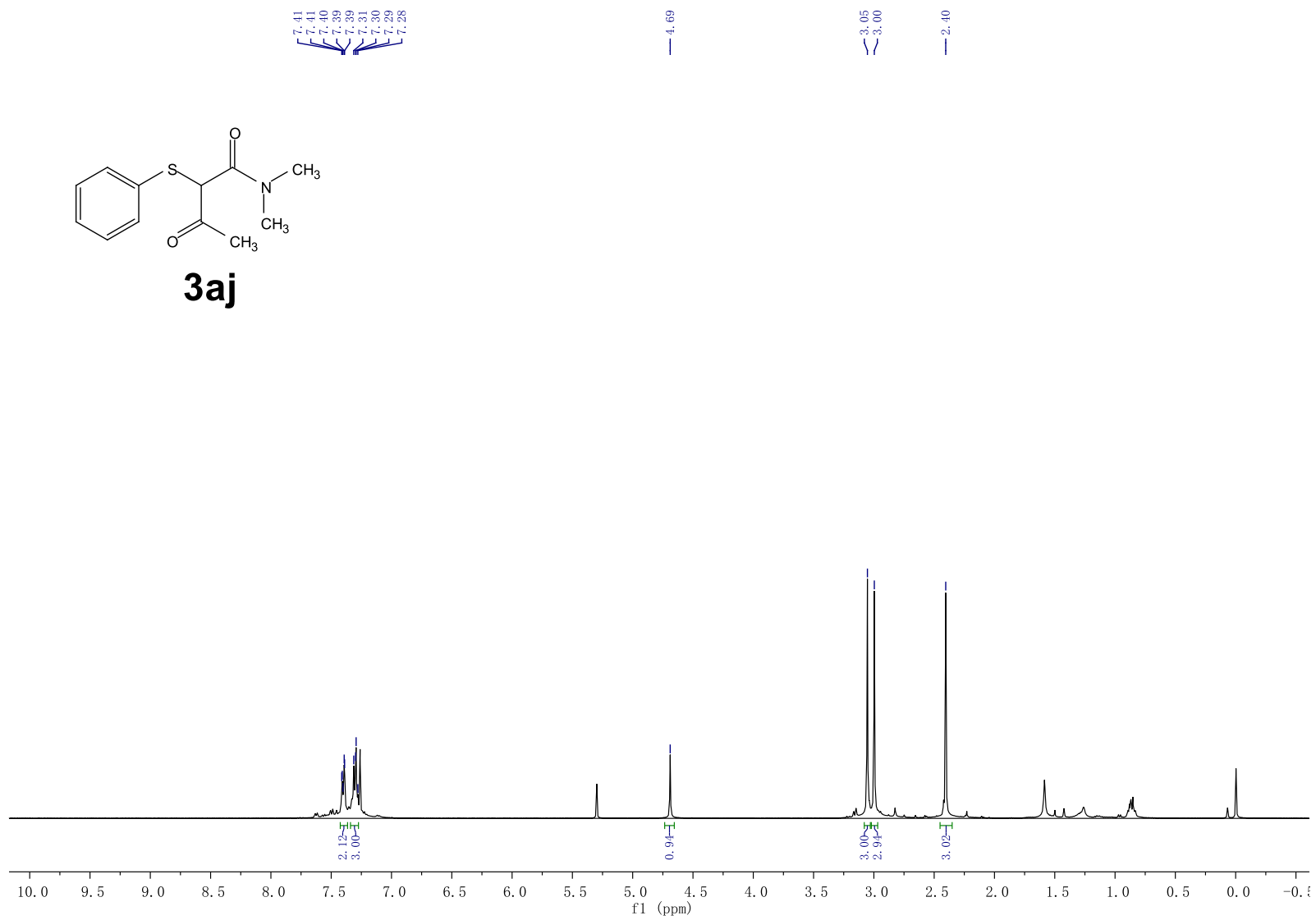


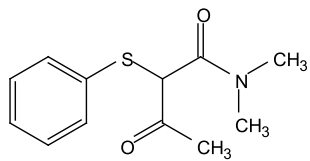
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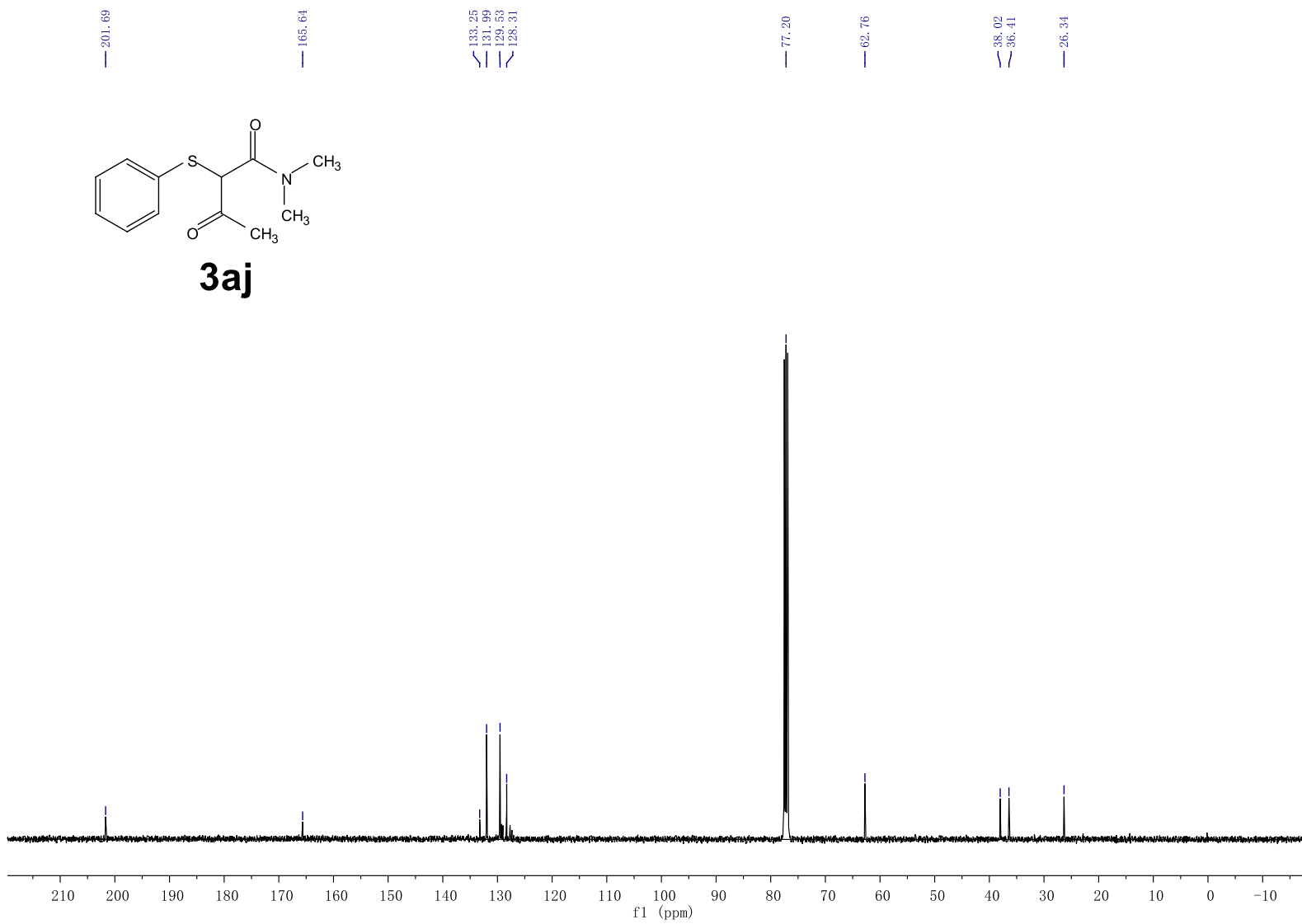


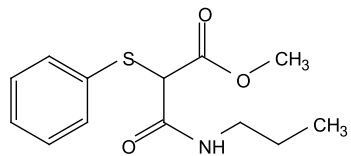
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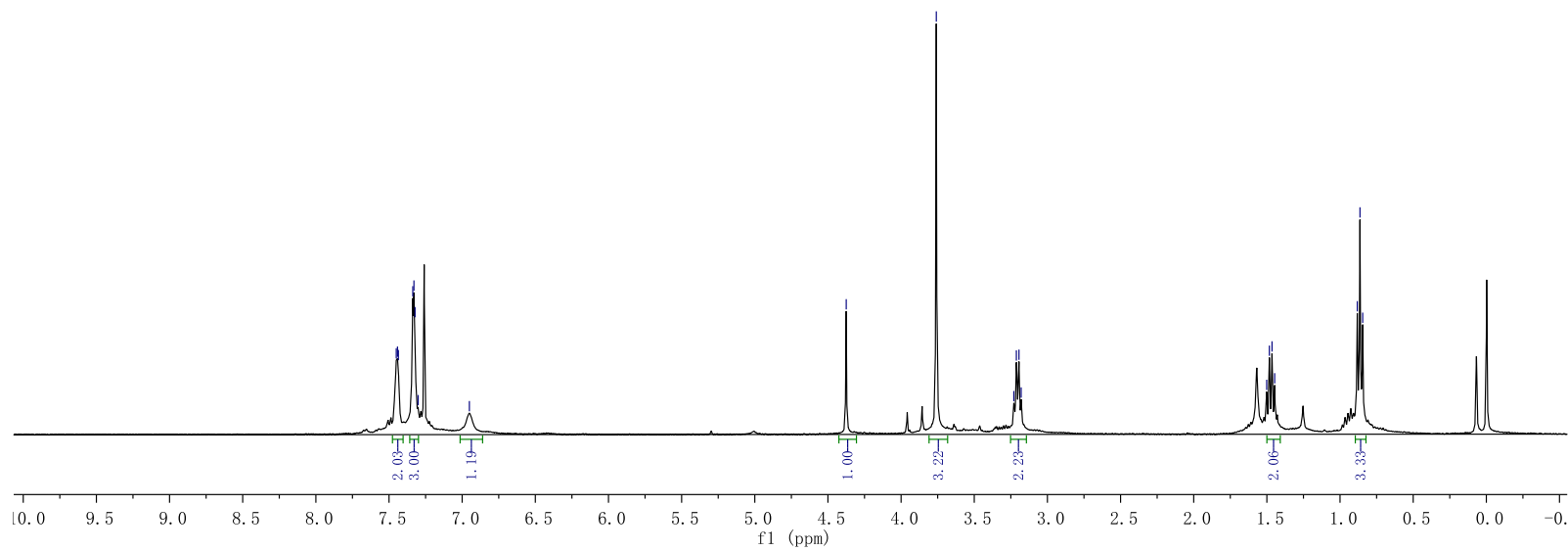
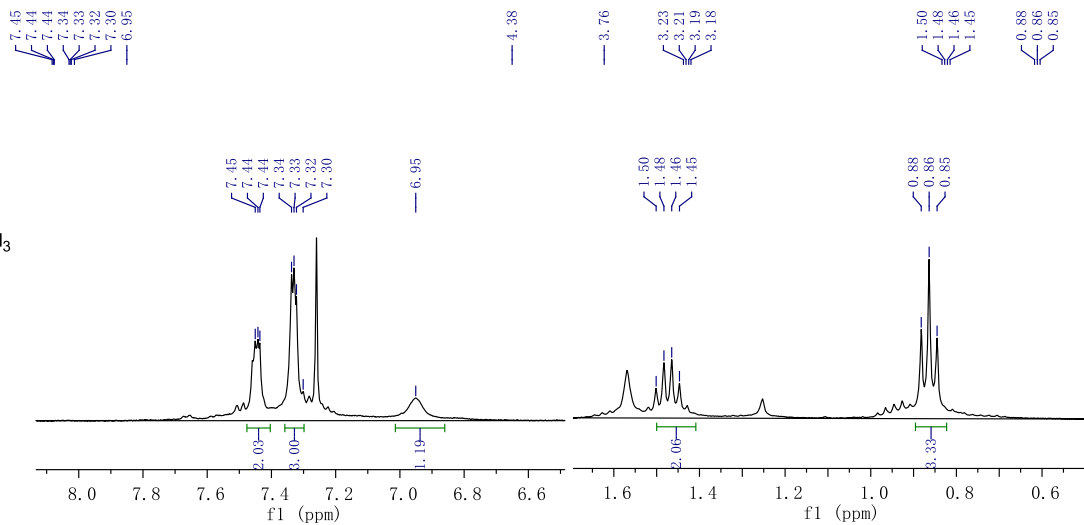


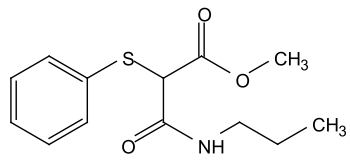
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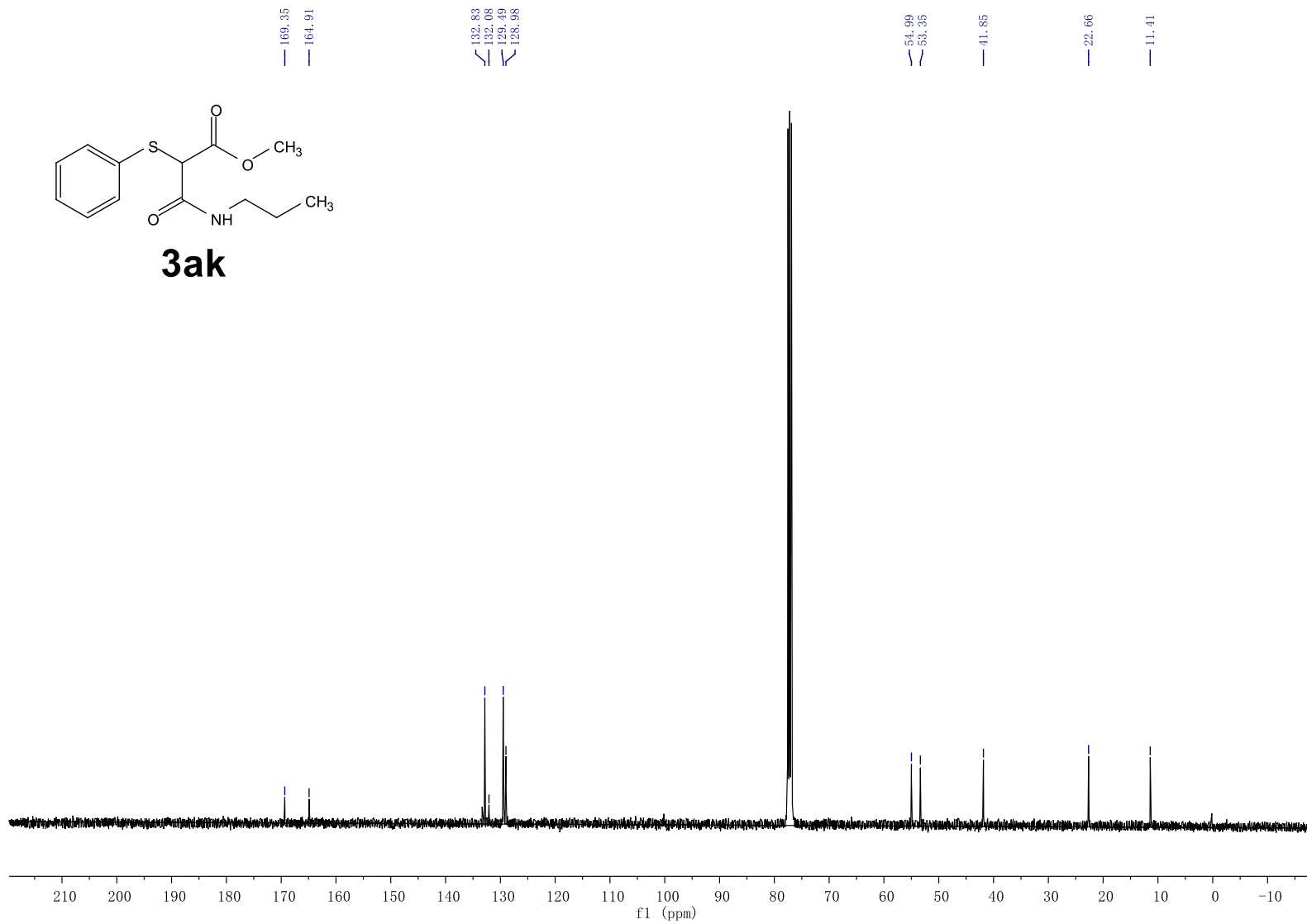


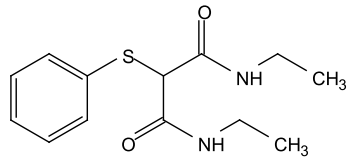
**3ak**





**3ak**





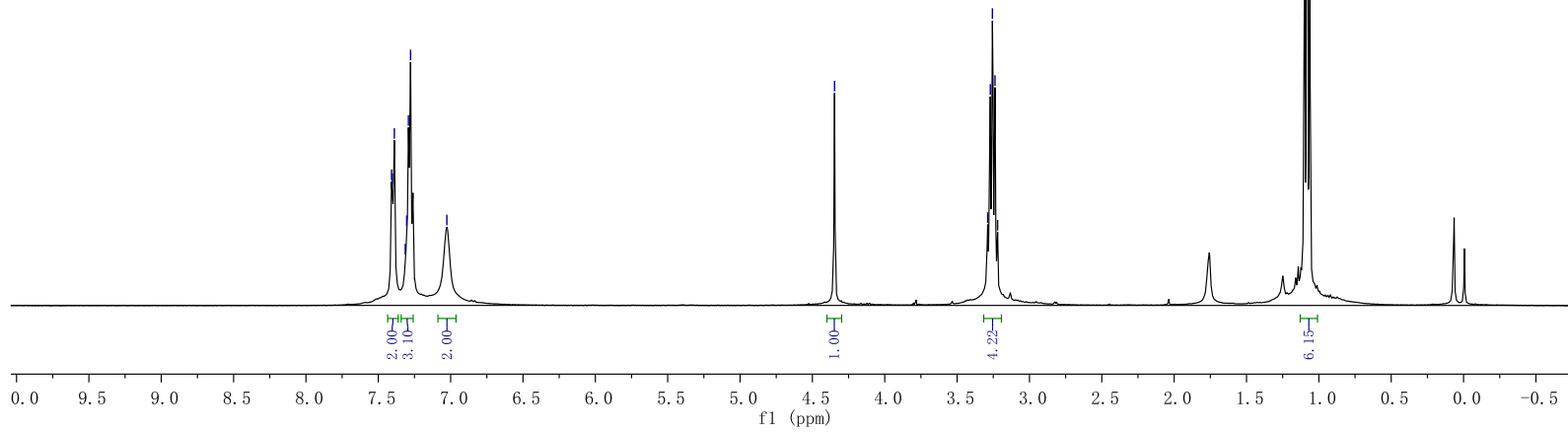
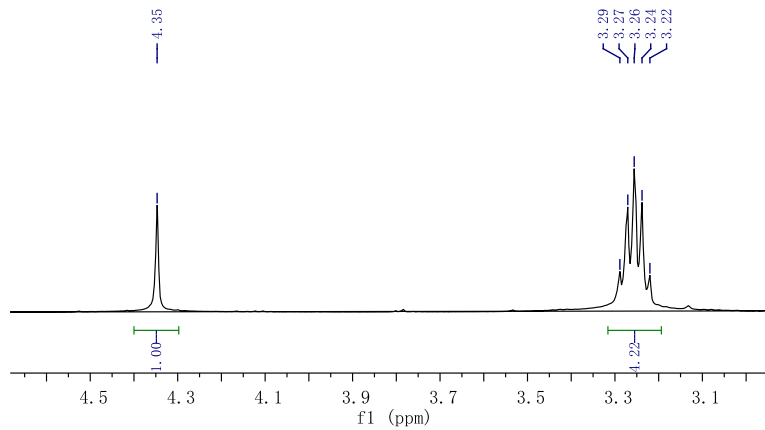
**3aI**

7.41  
7.40  
7.39  
7.31  
7.30  
7.29  
7.28  
7.03

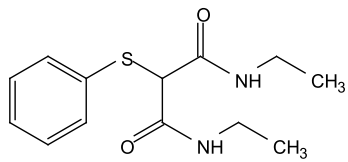
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3.29  
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3.26  
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3.22

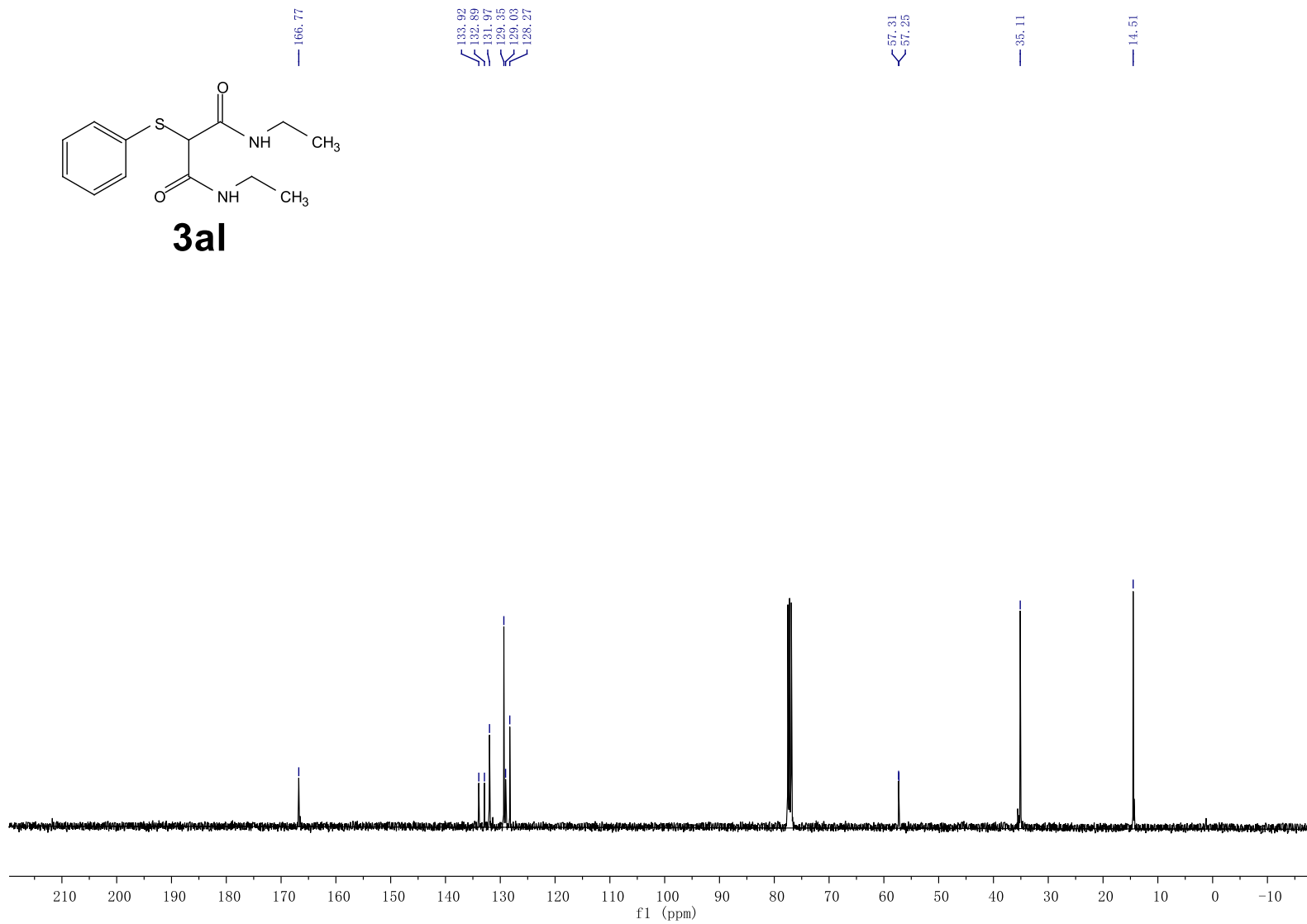
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1.08  
1.06

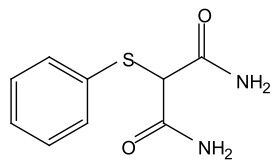






**3al**





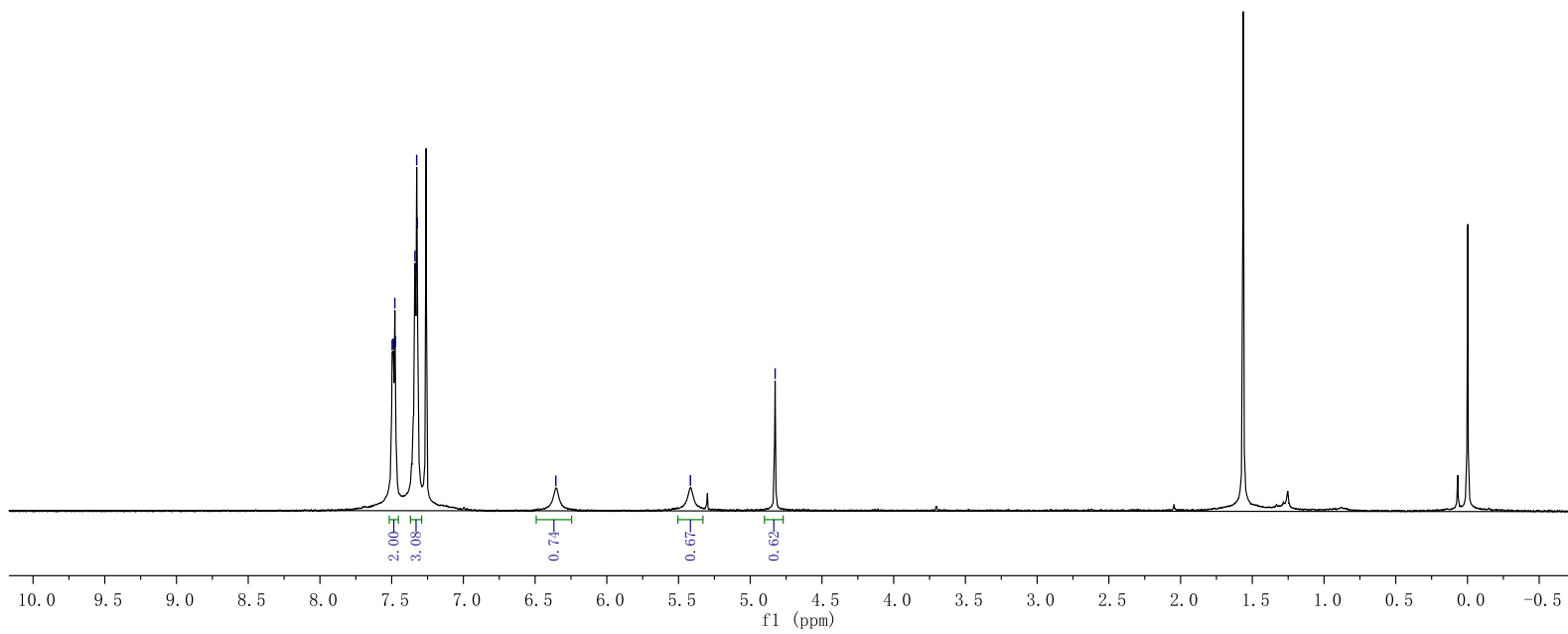
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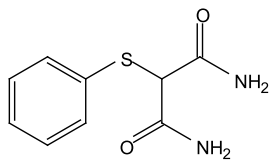
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7.48  
7.47  
7.34  
7.33  
7.32

6.36

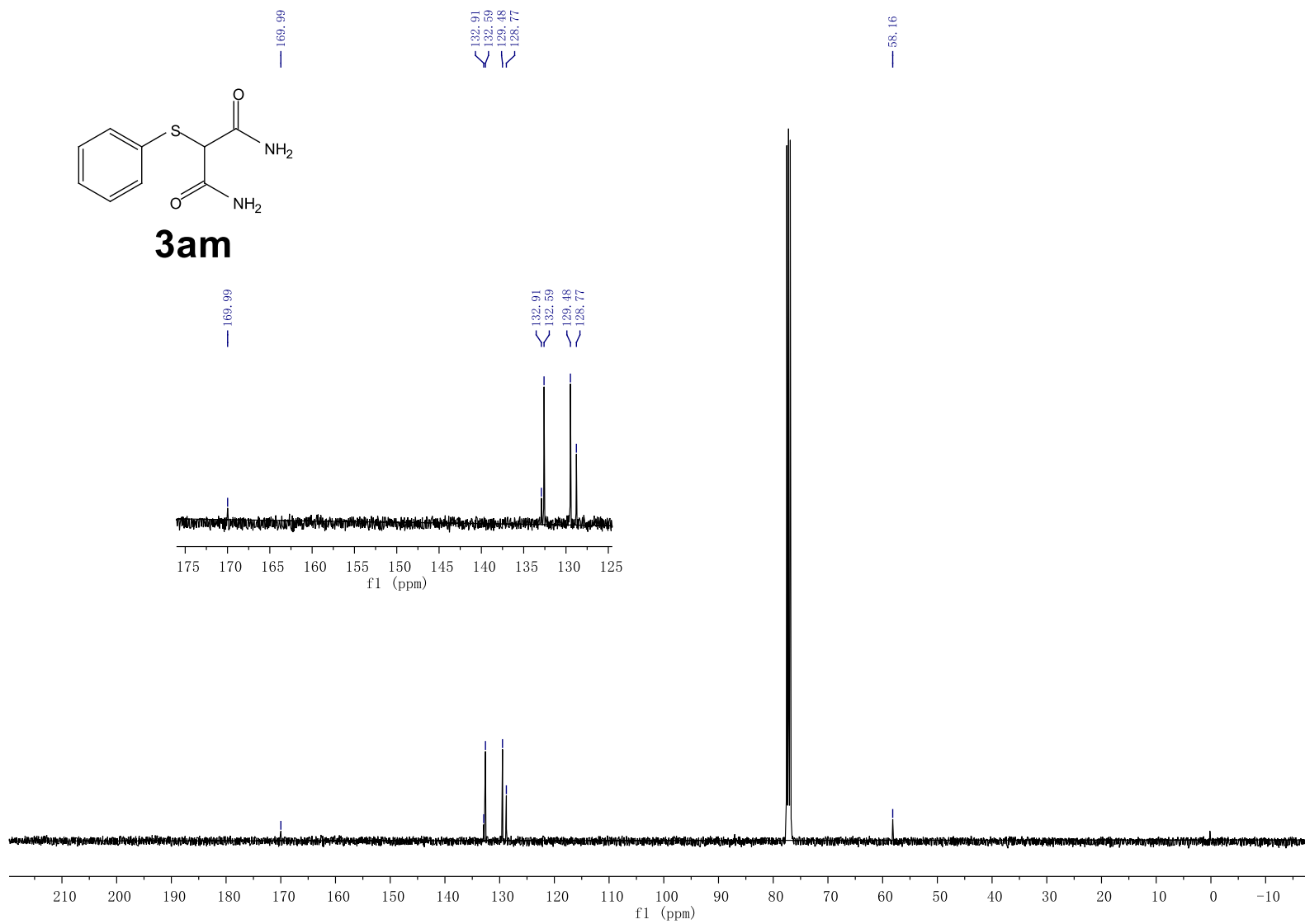
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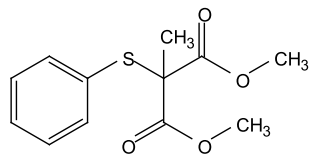
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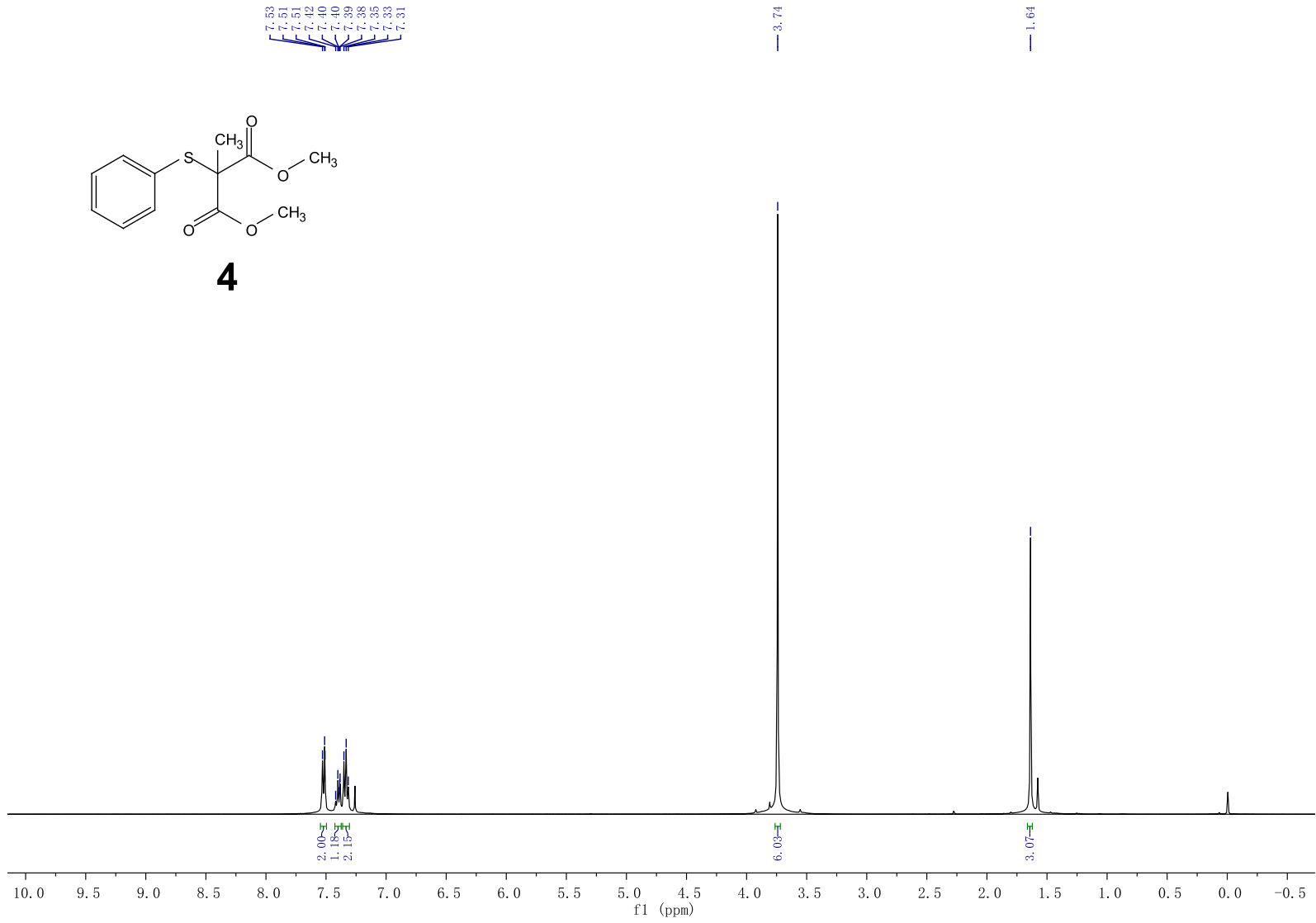


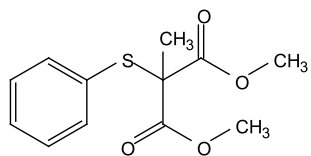
**3am**



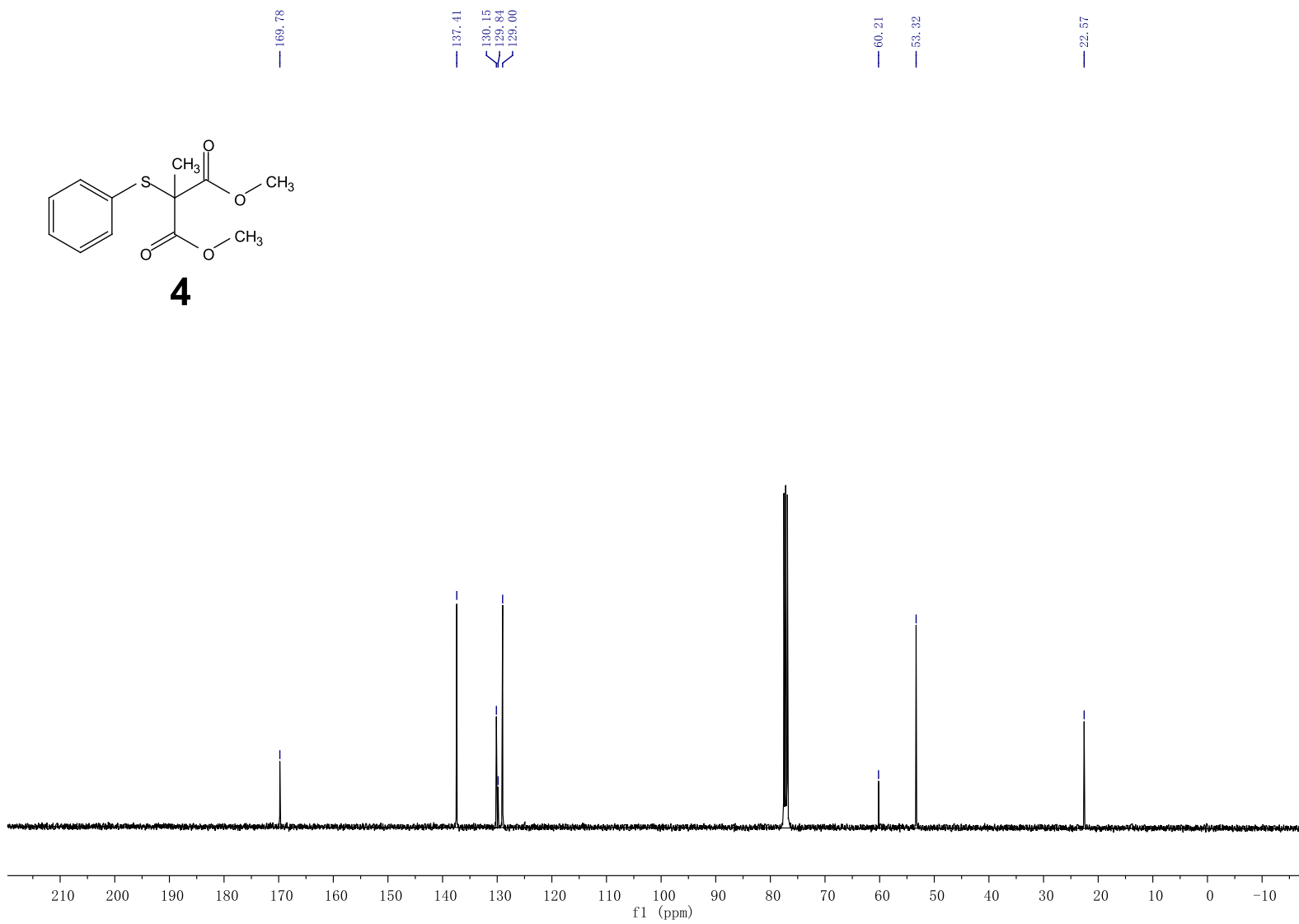


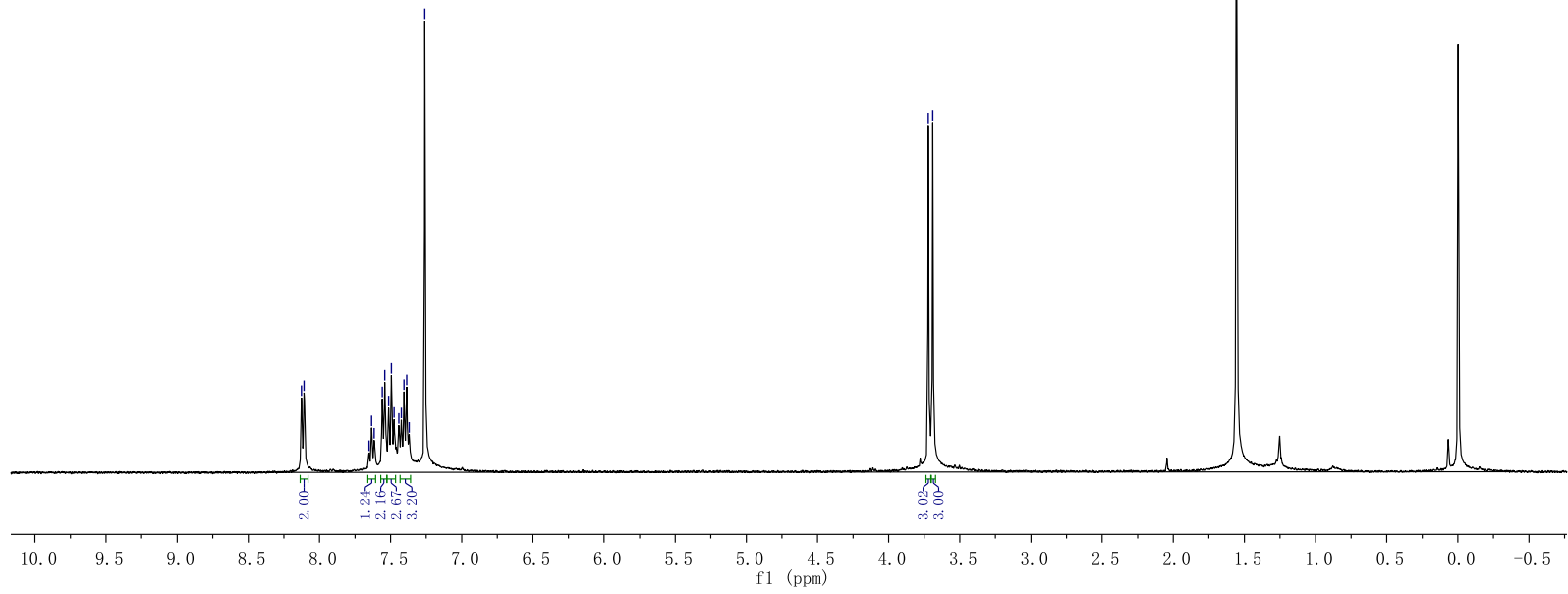
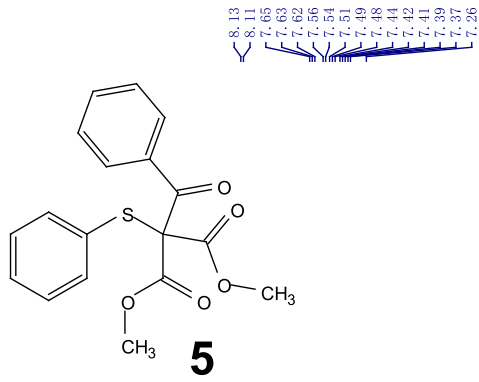
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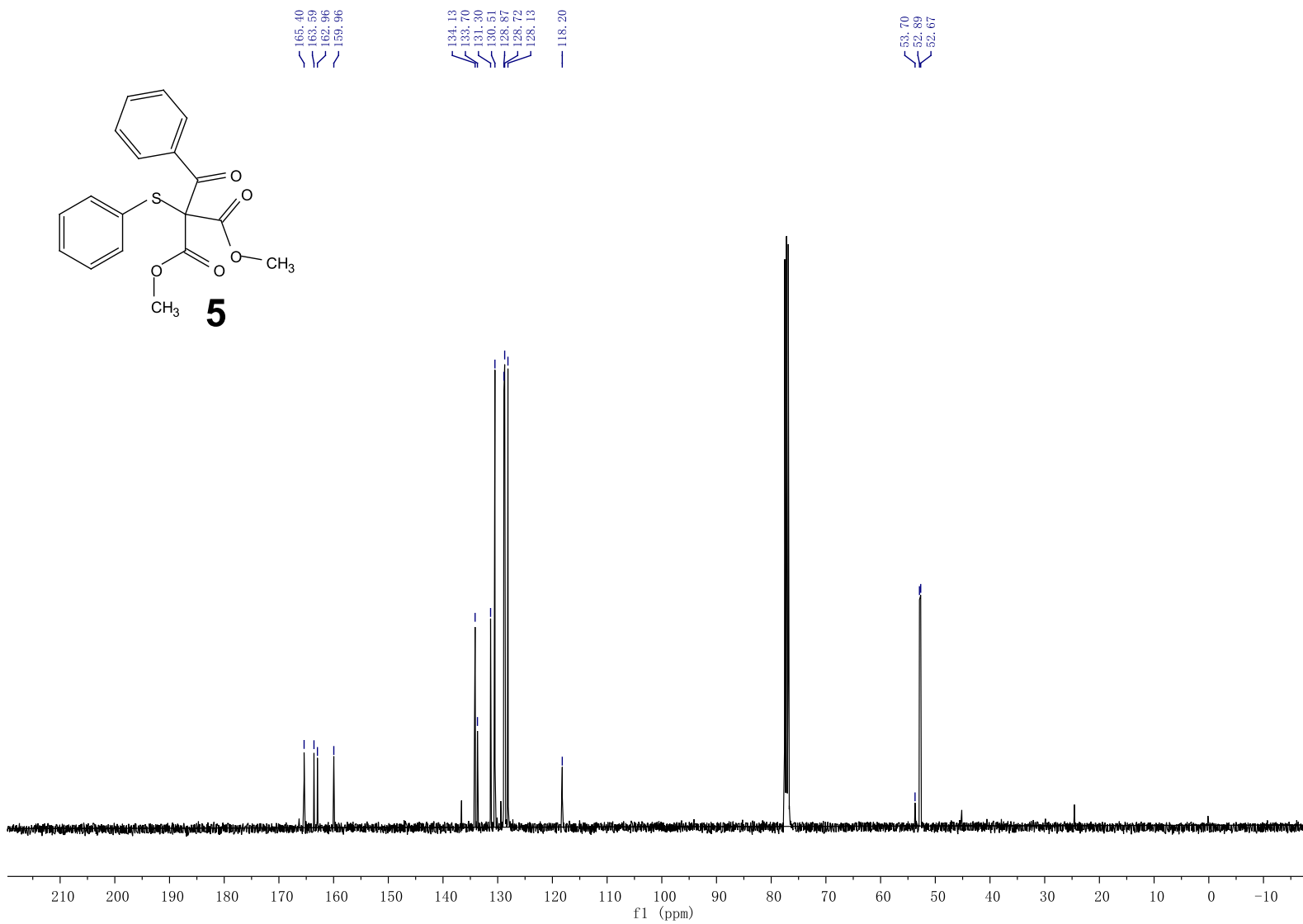
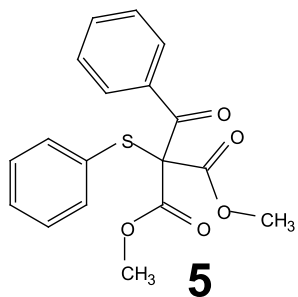


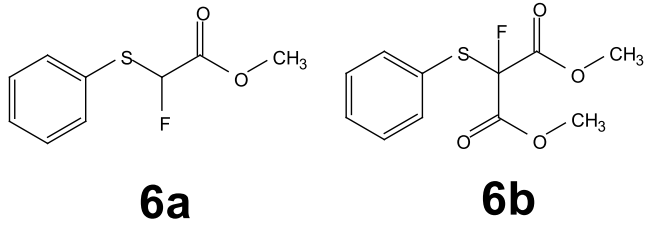


**4**

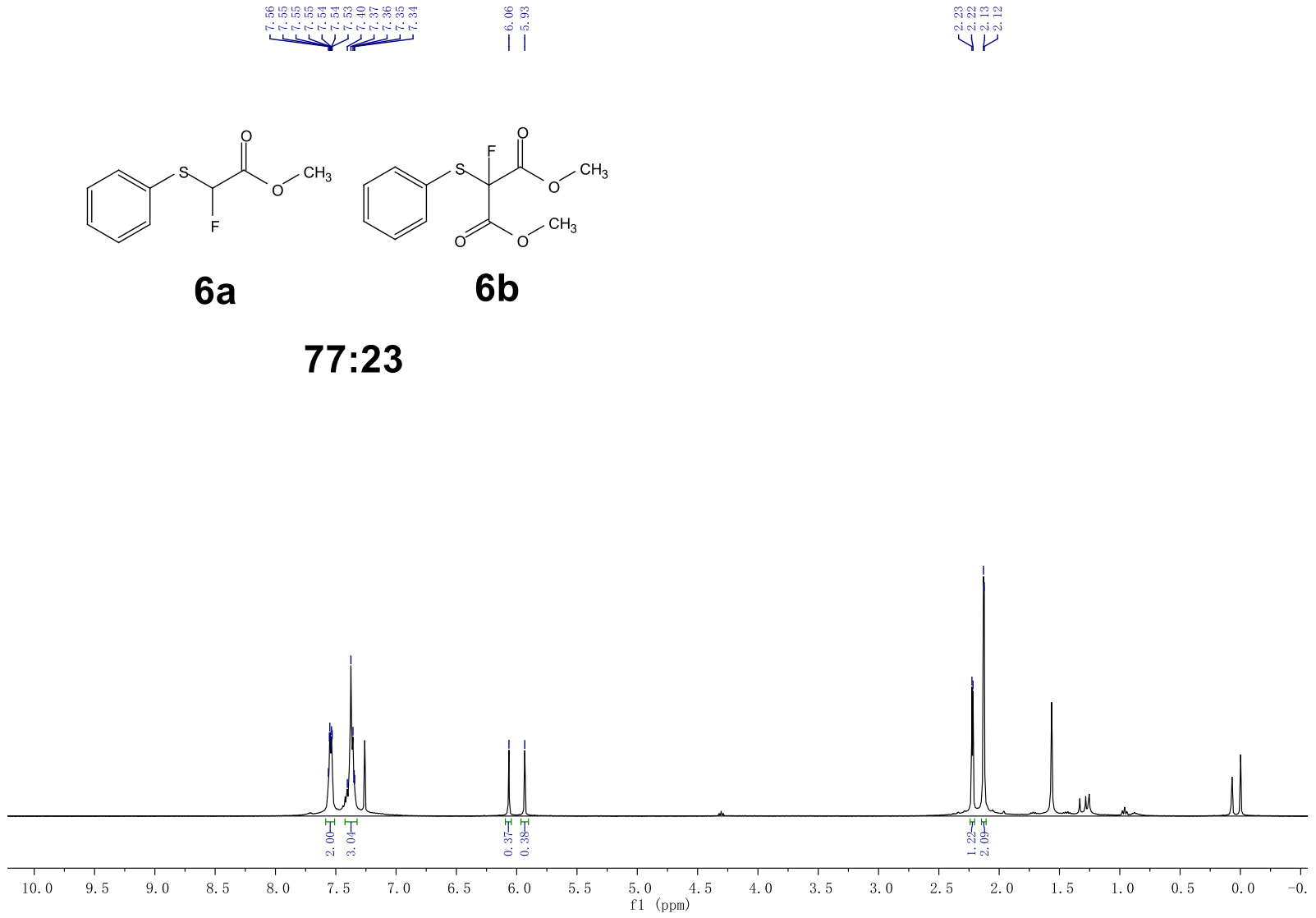




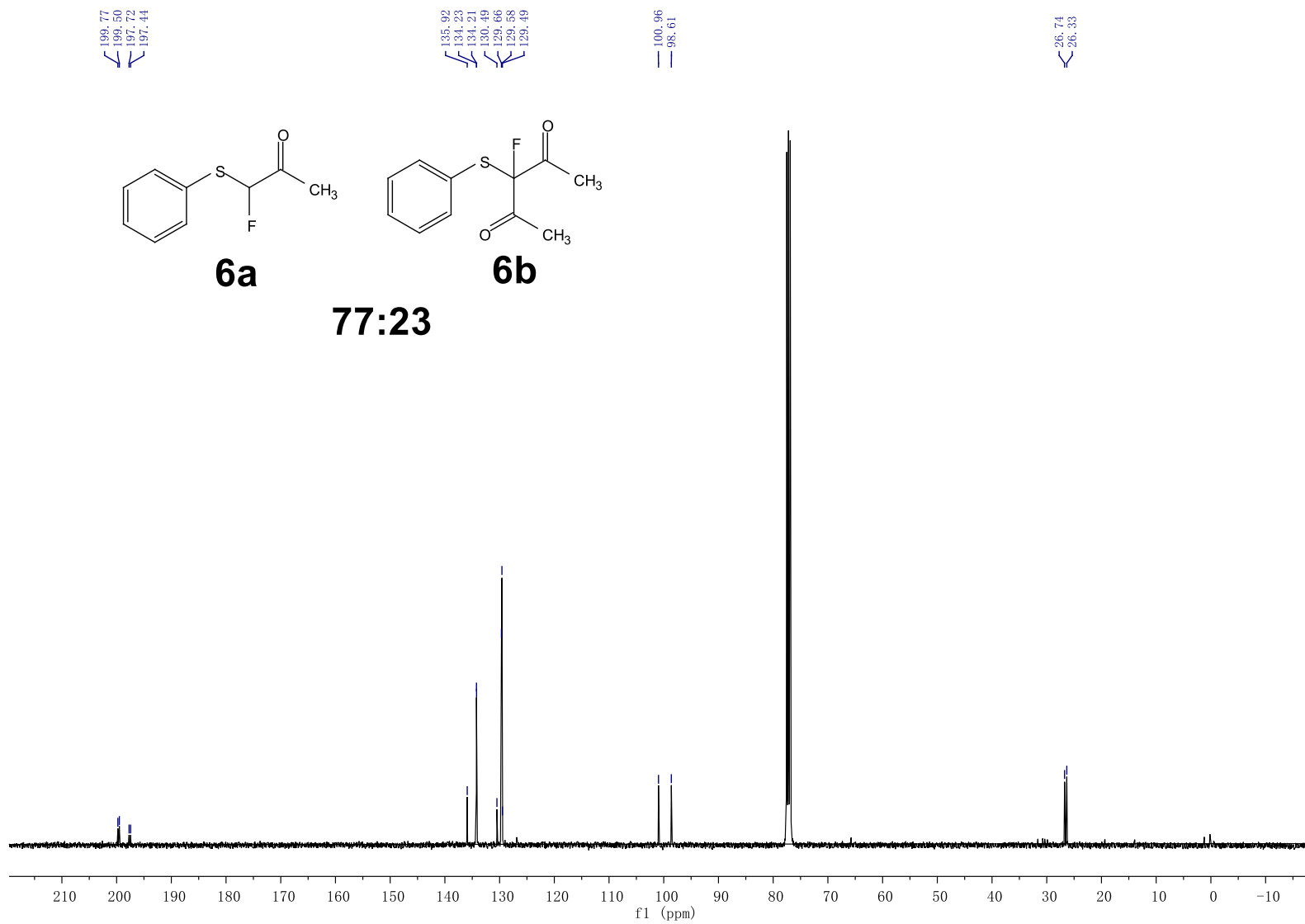


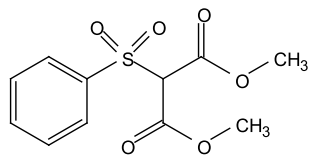


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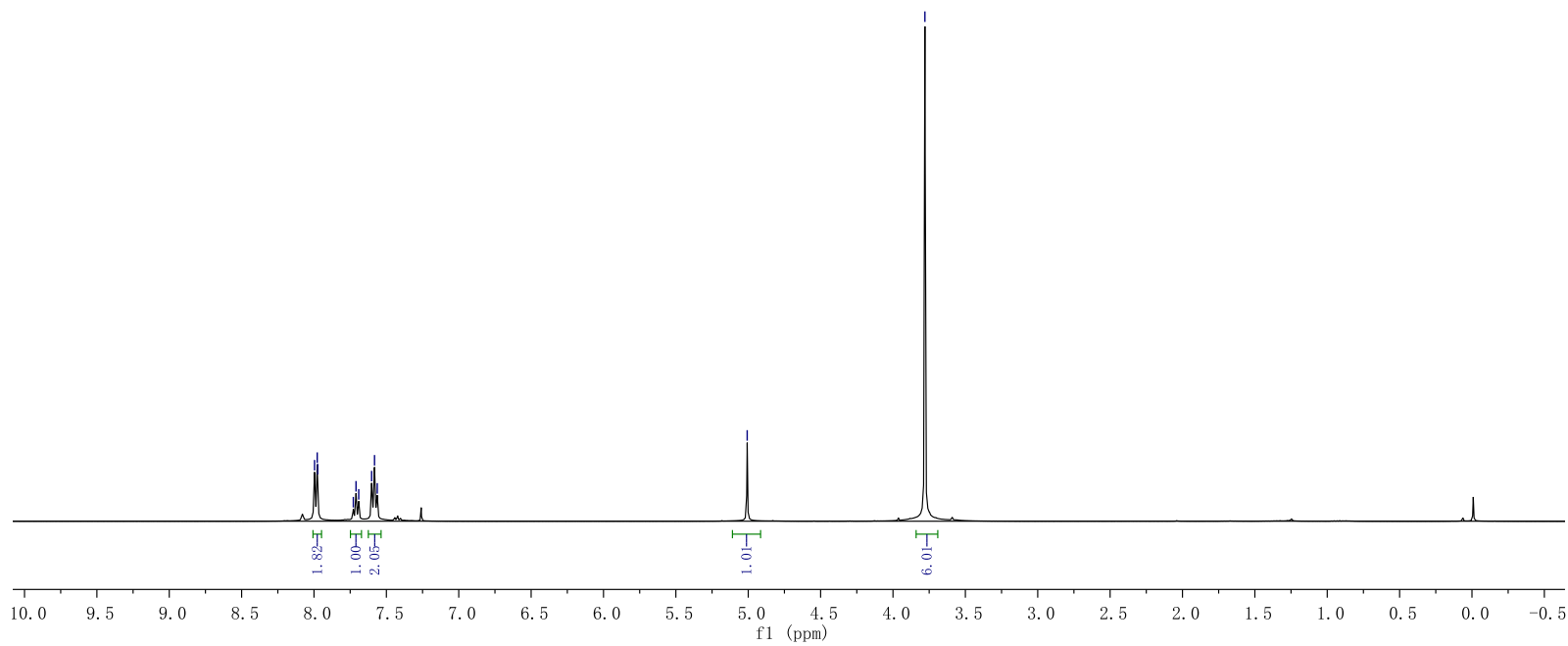


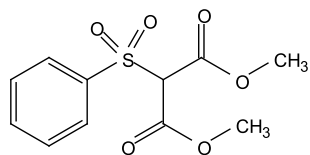
**7**

8.00  
7.98  
7.97  
7.73  
7.71  
7.69  
7.60  
7.58  
7.56

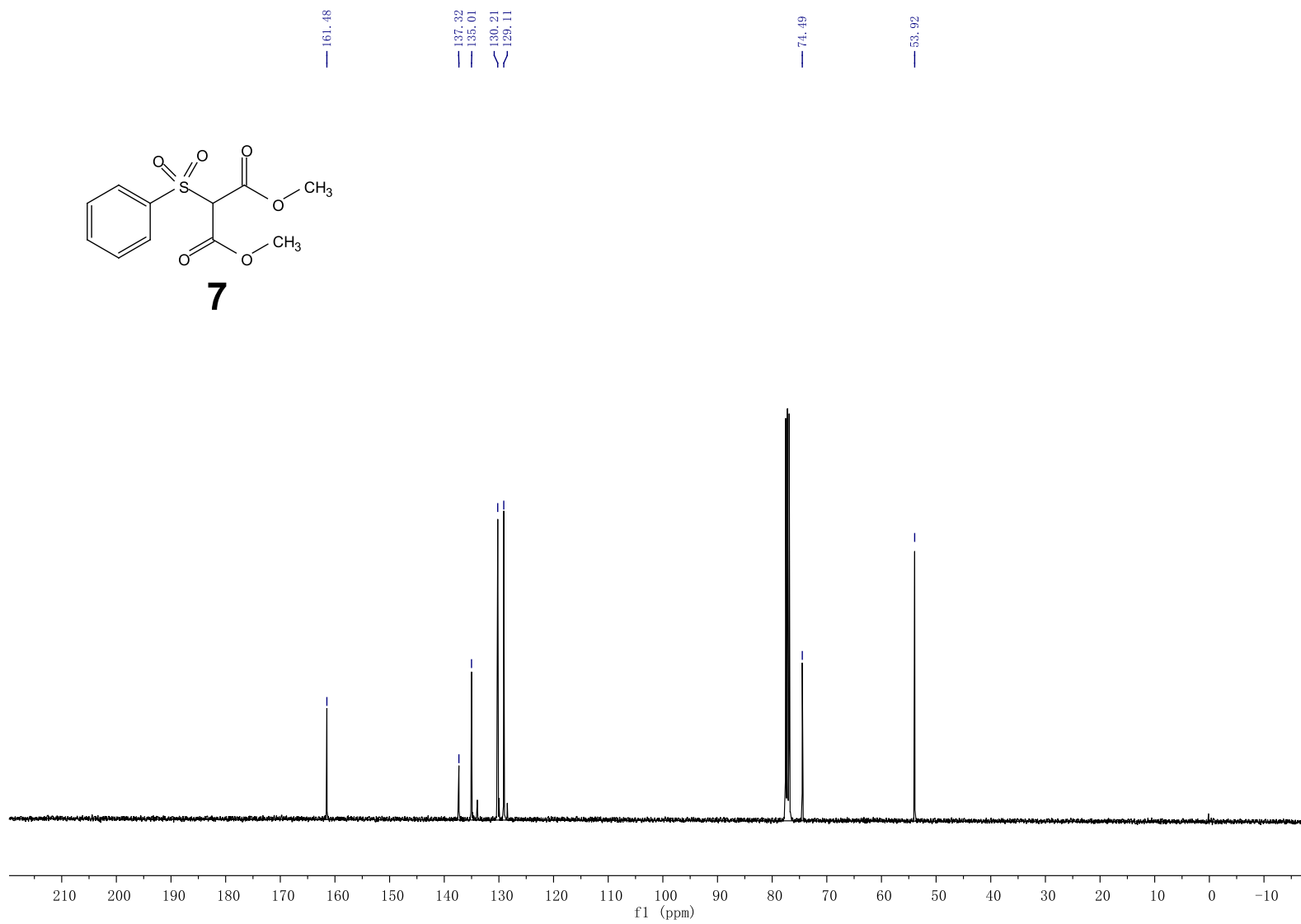
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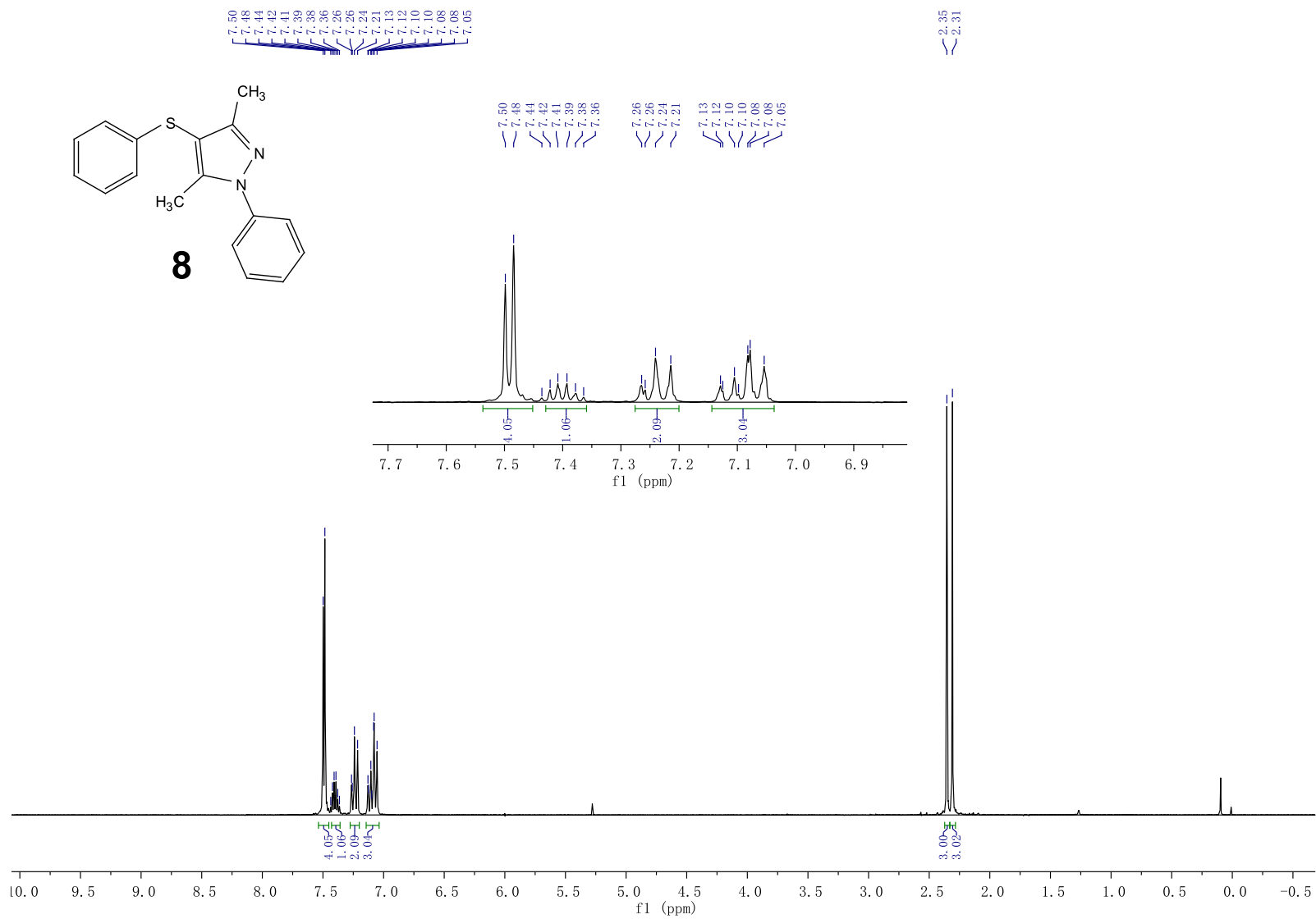
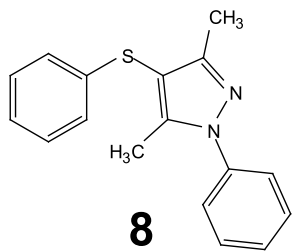
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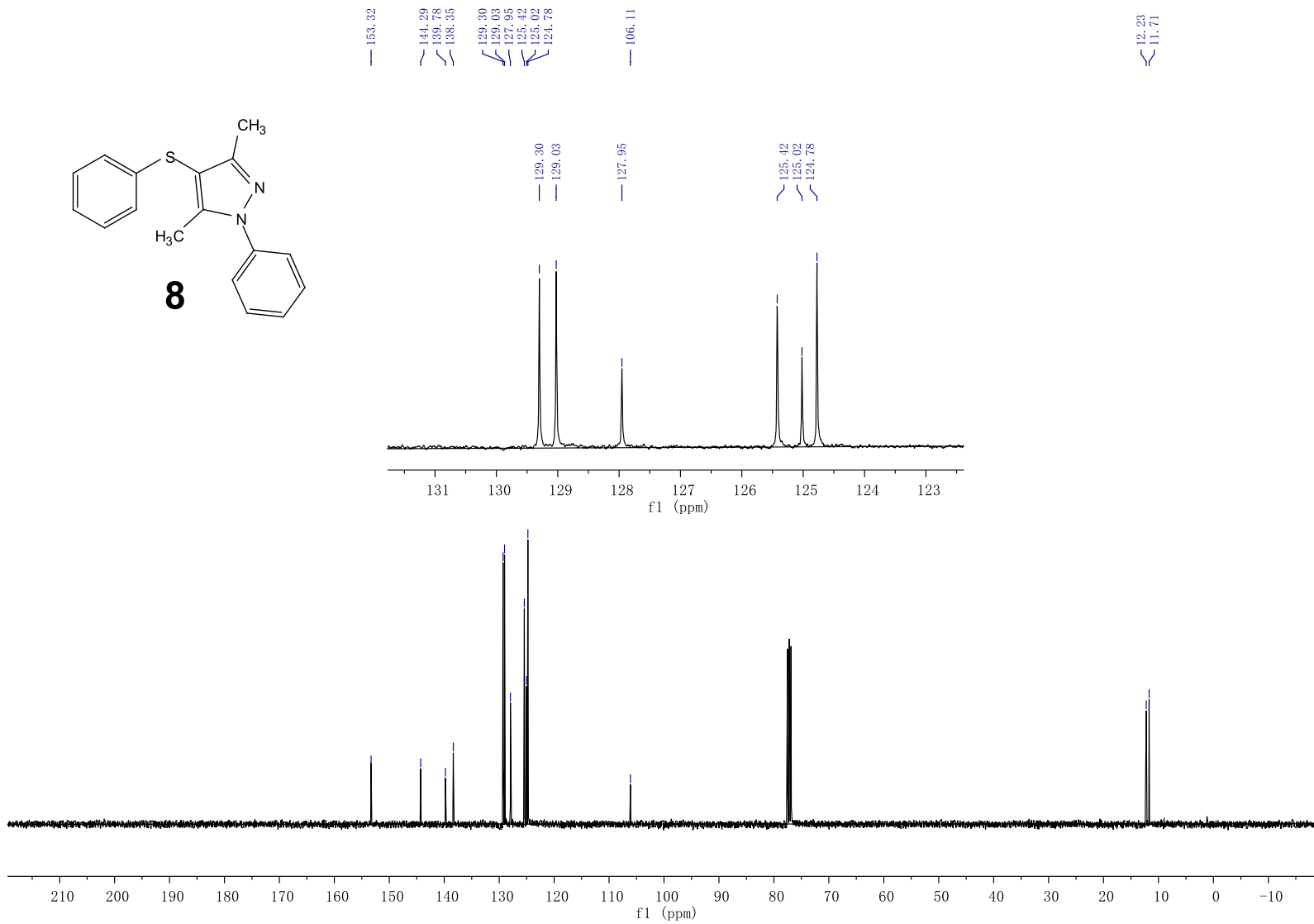
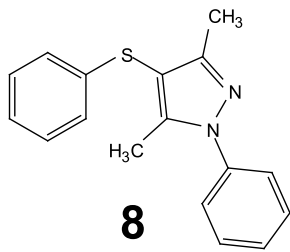


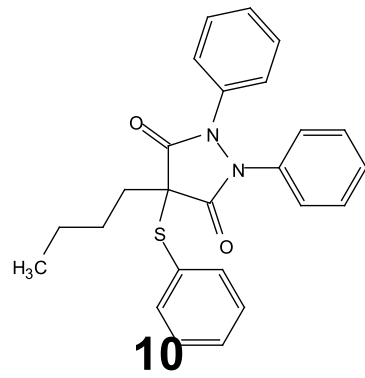


**7**









7.58  
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7.39  
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7.17  
7.15  
7.13  
7.10  
7.08  
7.06  
6.81  
6.79

2.17  
2.15  
2.13

1.41  
1.36  
1.35  
1.32  
1.24  
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0.87  
0.85

7.58  
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6.81  
6.79

