

## Supporting Information

### **Oxygen-Sulfur Rearrangement in the Reaction of Thiocarbamate Imidazolium Ylide with Arylaldehyde**

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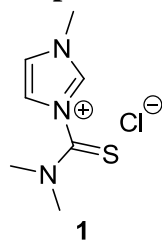
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## General

All the starting materials and solvents were commercially available.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded with a Bruker Avance III 400 MHz NMR spectrometer. HRMS were recorded with a Bruker Daltonics APEX II mass spectrometer. Solvents were dried by standard methods before use.

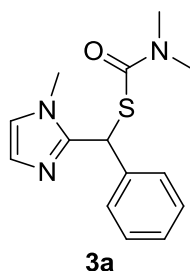
## Experimental details

### Preparation of *N*-thiocarbamate imidazolium salt **1**.



To a 500 ml of round bottom flask was added 39.4 g of 1-methylimidazole (0.48 mol), 46.9 g of dimethylthiocarbamoyl chloride (0.38 mol), and 250 ml of ethyl acetate. The mixture was allowed to reflux with stirring for 24 hours. After the reaction, the white precipitate was filtered, washed with ethyl acetate, and dried in vacuum to give 70.0 g of pure product **1** (**3-(dimethylcarbamothioyl)-1-methyl-1*H*-imidazol-3-ium chloride**). Yield: 90%. Mp. 197-198 °C.  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ , 25 °C):  $\delta$  = 3.30 (s, 3H), 3.46 (s, 3H), 3.96 (s, 3H), 8.04 (t,  $J$  = 1.6 Hz, 1H), 8.29 (t,  $J$  = 1.6 Hz, 1H), 10.11 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  36.3, 43.5, 45.0, 121.4, 123.6, 137.5, 172.6. HRMS: Calcd: for  $\text{C}_7\text{H}_{12}\text{N}_3\text{S}$  ( $[\text{M}-\text{Cl}]^+$ ) 170.0746, found: 170.0741.

### Reaction of **1** with benzaldehyde to afford 2-imidazolium alkylcarbamothioate **3a**.

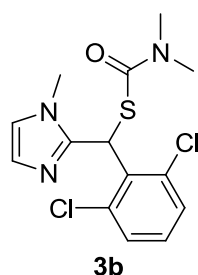


The imidazolium salt **1** (1.03 g, 5.0 mmol) was dissolved in 2 mL of dry DMF. To this solution was added benzaldehyde (0.51 mL, 5.0 mmol) and  $\text{Et}_3\text{N}$  (0.87 mL, 6.0 mmol) under nitrogen atmosphere. The reaction tube was sealed and the mixture was stirred at 30 for 12 hours. Then water (10 mL) was added to quench the reaction, and the product was extracted with ethyl acetate (3×10 mL). The combined extracts were washed with water (2×10 mL) and brine (2×10 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ ,

and concentrated. The residue was purified by chromatography on silica gel with ethyl acetate/petroleum ether (1:3) to give 1.30 g of the product **3a** (*S*-(1-methyl-1*H*-imidazol-2-yl)(phenyl)methyl dimethylcarbamothioate) as white powder. Yield: 95%. Mp. 114-116 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ = 2.98 (s, 6H), 3.58 (s, 3H), 5.97 (s, 1H), 6.79 (d, *J* = 1.2 Hz, 1H), 7.03 (d, *J* = 1.2 Hz, 1H), 7.22-7.46 (m, 3H), 7.48 (d, *J* = 1.2 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C): δ = 32.9, 36.6, 36.8, 44.9, 121.1, 127.6, 127.7, 128.4, 128.7, 139.0, 146.6, 167.0. HRMS: Calcd: for C<sub>14</sub>H<sub>18</sub>N<sub>3</sub>OS ([M+H]<sup>+</sup>) 276.1165, found: 276.1169.

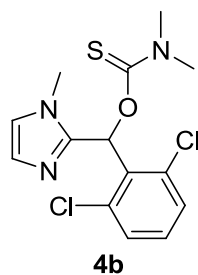
The procedure for achieving **3b-3v**, **4b**, **4w**, and **4x** are similar to that of **3a**, with some variations on reaction temperature and reaction time when necessary.

***S*-(2,6-dichlorophenyl)(1-methyl-1*H*-imidazol-2-yl)methyl dimethylcarbamothioate (**3b**)**



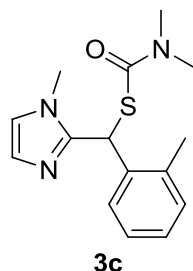
**3b** was obtained as white powder from the reaction of **1** with 2,6-dichlorobenzaldehyde at 100 °C for 12 h. Yield: 64%. Mp. 173-174 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ = 3.04 (s, 6H), 3.55 (s, 3H), 6.82 (d, *J* = 1.2 Hz, 1H), 6.96 (d, *J* = 1.2 Hz, 1H), 7.06 (s, 1H), 7.14-7.18 (m, 1H), 7.34 (s, 1H), 7.36 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C): δ = 33.2, 36.6, 37.3, 42.4, 122.3, 127.5, 129.2, 135.3, 143.8, 166.8. HRMS: Calcd for C<sub>14</sub>H<sub>16</sub>Cl<sub>2</sub>N<sub>3</sub>OS ([M+H]<sup>+</sup>): 344.0386, found: 344.0392.

***O*-(2,6-dichlorophenyl)(1-methyl-1*H*-imidazol-2-yl)methyl dimethylcarbamothioate (**4b**)**



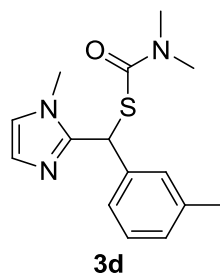
**4b** was obtained as white powder from the reaction of **1** with 2,6-dichlorobenzaldehyde at 30 °C for 12 h. Yield: 99%. Mp. 152-153 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ = 3.26 (s, 3H), 3.38 (s, 3H), 3.71 (s, 3H), 6.93 (d, *J* = 1.2 Hz, 1H), 7.01 (d, *J* = 1.2 Hz, 1H), 7.18-7.26 (m, 1H), 7.34 (s, 1H), 7.36 (s, 1H), 8.34 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C): δ = 33.6, 38.5, 43.4, 73.3, 122.6, 128.3, 129.4, 129.9, 132.5, 135.7, 142.4, 186.2. HRMS: Calcd for C<sub>14</sub>H<sub>15</sub>Cl<sub>2</sub>N<sub>3</sub>OS ([M+H]<sup>+</sup>): 344.0386, found: 344.0392.

***S*-(1-methyl-1*H*-imidazol-2-yl)(*o*-tolyl)methyl dimethylcarbamothioate (3c)**



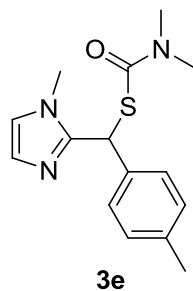
**3c** was obtained as white powder from the reaction of **1** with 2-methylbenzaldehyde at 30 °C for 12 h. Yield: 80%. Mp. 106-108 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ = 2.48 (s, 3H), 2.98 (s, 6H), 3.54 (s, 3H), 6.10 (s, 1H), 6.79 (d, *J* = 1.2 Hz, 1H), 7.03 (d, *J* = 1.2 Hz, 1H), 7.13-7.18 (m, 3H), 7.42-7.44 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C): δ = 19.5, 32.8, 36.7, 36.8, 41.9, 121.1, 126.5, 127.6, 127.8, 129.4, 130.6, 135.5, 135.9, 147.0, 167.1. HRMS: Calcd for C<sub>15</sub>H<sub>20</sub>N<sub>3</sub>OS ([M+H]<sup>+</sup>): 290.1322, found: 290.1329.

***S*-(1-methyl-1*H*-imidazol-2-yl)(*m*-tolyl)methyl dimethylcarbamothioate (3d)**



**3d** was obtained as white powder from the reaction of **1** with 3-methylbenzaldehyde at 30 °C for 12 h. Yield: 89%. Mp. 91-93 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ = 2.31 (s, 3H), 2.97 (s, 6H), 3.58 (d, *J* = 3.6 Hz, 3H), 5.93 (s, 3H), 6.78 (s, 1H), 7.02-7.06 (m, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.26-7.28 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C): δ = 21.4, 32.9, 36.7, 36.8, 44.9, 121.0, 125.5, 127.7, 128.5, 128.6, 129.0, 138.4, 138.9, 146.8, 167.1. HRMS: Calcd for C<sub>15</sub>H<sub>20</sub>N<sub>3</sub>OS ([M+H]<sup>+</sup>): 290.1322, found: 290.1331.

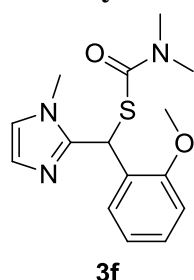
***S*-(1-methyl-1*H*-imidazol-2-yl)(*p*-tolyl)methyl dimethylcarbamothioate (3e)**



**3e** was obtained as white powder from the reaction of **1** with 4-methylbenzaldehyde at 30 °C for 12 h. Yield: 86%. Mp. 100-103 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ

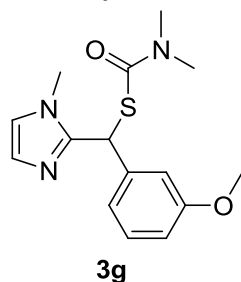
= 2.30 (s, 3H), 2.97 (s, 6H), 3.58 (s, 3H), 5.94 (s, 1H), 6.78 (d,  $J = 1.2$  Hz, 1H), 7.02 (d,  $J = 1.2$  Hz, 1H), 7.11 (d,  $J = 8.0$  Hz, 2H), 7.36 (d,  $J = 8.0$  Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 21.1, 32.9, 36.6, 36.8, 44.7, 121.0, 127.7, 128.3, 129.4, 136.1, 137.4, 146.7, 167.1$ . HRMS: Calcd for  $\text{C}_{15}\text{H}_{20}\text{N}_3\text{OS}$  ( $[\text{M}+\text{H}]^+$ ): 290.1322, found: 290.1330.

***S*-(2-methoxyphenyl)(1-methyl-1*H*-imidazol-2-yl)methyl dimethylcarbamothioate (3f)**



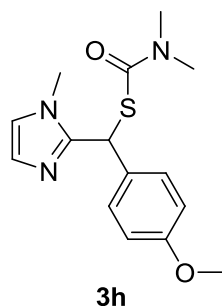
**3f** was obtained as white powder from the reaction of **1** with 2-methoxybenzaldehyde at 30 °C for 12 h. Yield: 76%. Mp. 128-130 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 2.97$  (s, 6H), 3.67 (s, 3H), 3.89 (s, 3H), 6.41 (s, 1H), 6.73 (d,  $J = 1.2$  Hz, 1H), 6.86-6.95 (m, 2H), 6.99 (d,  $J = 1.2$  Hz, 1H), 7.20-7.25 (m, 1H), 7.62-7.64 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 32.8, 36.7, 37.5, 55.8, 110.6, 120.6, 121.0, 121.1, 126.2, 127.7, 128.9, 130.4, 147.6, 155.6, 167.4$ . HRMS: Calcd for  $\text{C}_{15}\text{H}_{20}\text{N}_3\text{O}_2\text{S}$  ( $[\text{M}+\text{H}]^+$ ): 306.1271, found: 306.1278.

***S*-(3-methoxyphenyl)(1-methyl-1*H*-imidazol-2-yl)methyl dimethylcarbamothioate (3g)**



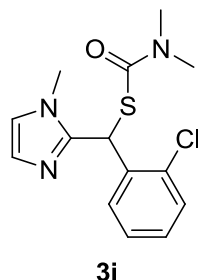
**3g** was obtained as white powder from the reaction of **1** with 3-methoxybenzaldehyde at 30 °C for 12 h. Yield: 91%. Mp. 60-63 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 2.98$  (s, 6H), 3.58 (s, 3H), 3.77 (s, 3H), 5.95 (s, 1H), 6.77-6.79 (m, 2H), 7.01-7.04 (m, 3H), 7.19-7.23 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 32.9, 36.7, 36.8, 55.2, 113.4, 113.8, 120.6, 121.1, 127.6, 129.7, 140.5, 146.6, 159.8, 167.0$ . HRMS: Calcd for  $\text{C}_{15}\text{H}_{20}\text{N}_3\text{O}_2\text{S}$  ( $[\text{M}+\text{H}]^+$ ): 306.1271, found: 306.1275.

***S*-(4-methoxyphenyl)(1-methyl-1*H*-imidazol-2-yl)methyl dimethylcarbamothioate (3h)**



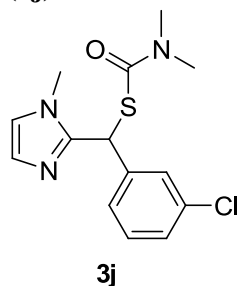
**3h** was obtained as white powder from the reaction of **1** with 4-methoxybenzaldehyde at 30 °C for 12 h. Yield: 48%. Mp. 101-104 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 2.97 (s, 3H), 3.57 (s, 3H), 3.76 (s, 3H), 5.93 (s, 1H), 6.78 (d,  $J$  = 1.2 Hz, 1H), 6.83 (d,  $J$  = 8.8 Hz, 2H), 7.01 (d,  $J$  = 1.2 Hz, 1H), 7.40 (d,  $J$  = 8.8 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 32.9, 36.6, 44.4, 55.2, 114.0, 121.0, 127.6, 129.6, 131.1, 146.8, 159.0, 167.2. HRMS: Calcd for C<sub>15</sub>H<sub>20</sub>N<sub>3</sub>O<sub>2</sub>S ([M+H]<sup>+</sup>): 306.1271, found: 306.1275.

**S-(2-chlorophenyl)(1-methyl-1H-imidazol-2-yl)methyl dimethylcarbamothioate (3i)**



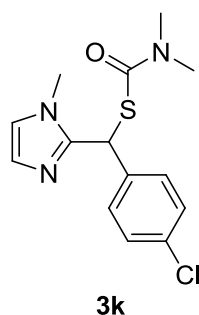
**3i** was obtained as white powder from the reaction of **1** with 2-chlorobenzaldehyde at 60 °C for 24 h. Yield: 82%. Mp. 144-145 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 2.98 (s, 6H), 3.71 (s, 3H), 6.43 (s, 1H), 6.79 (d,  $J$  = 0.8 Hz, 1H), 7.02 (d,  $J$  = 0.8 Hz, 1H), 7.18-7.28 (m, 2H), 7.36-7.38 (m, 1H), 7.77-7.79 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 33.0, 36.7, 36.8, 41.3, 121.1, 127.3, 127.9, 129.0, 129.5, 131.2, 132.7, 135.7, 146.3, 166.5. HRMS: Calcd for C<sub>14</sub>H<sub>17</sub>ClN<sub>3</sub>OS ([M+H]<sup>+</sup>): 310.0775, found: 310.0784.

**S-(3-chlorophenyl)(1-methyl-1H-imidazol-2-yl)methyl dimethylcarbamothioate (3j)**



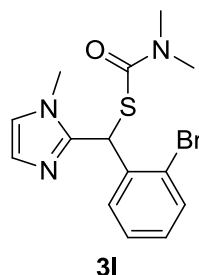
**3i** was obtained as white powder from the reaction of **1** with 3-chlorobenzaldehyde at 30 °C for 12 h. Yield: 94%. Mp. 111-113 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ = 2.98 (s, 6H), 3.60 (s, 3H), 5.95 (s, 1H), 6.81 (d, *J* = 1.2 Hz, 1H), 7.03 (d, *J* = 1.2 Hz, 1H), 7.20-7.26 (m, 2H), 7.36-7.39 (m, 1H), 7.49 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C): δ = 33.0, 36.7, 36.9, 44.3, 121.2, 126.7, 127.9, 127.9, 128.5, 129.9, 134.4, 141.3, 145.9, 166.6. HRMS: Calcd for C<sub>14</sub>H<sub>17</sub>ClN<sub>3</sub>OS ([M+H]<sup>+</sup>): 310.0775, found: 310.0785.

**S-(4-chlorophenyl)(1-methyl-1*H*-imidazol-2-yl)methyl dimethylcarbamothioate (3k)**



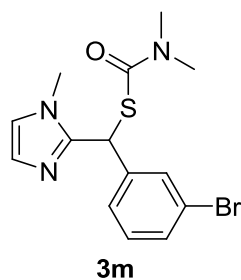
**3k** was obtained as white powder from the reaction of **1** with 4-chlorobenzaldehyde at 30 °C for 12 h. Yield: 98%. Mp. 108-110 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ = 2.99 (s, 6H), 3.59 (s, 3H), 5.94 (s, 1H), 6.80 (s, 1H), 7.02 (s, 1H), 7.26-7.29 (m, 2H), 7.44 (d, *J* = 8.8 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C): δ = 33.0, 36.7, 36.8, 44.2, 121.3, 127.8, 128.8, 129.9, 133.5, 137.9, 146.0, 166.7. HRMS: Calcd for C<sub>14</sub>H<sub>17</sub>ClN<sub>3</sub>OS ([M+H]<sup>+</sup>): 310.0775, found: 310.0779.

**S-(2-bromophenyl)(1-methyl-1*H*-imidazol-2-yl)methyl dimethylcarbamothioate (3l)**



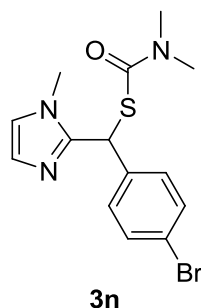
**3l** was obtained as white powder from the reaction of **1** with 2-bromobenzaldehyde at 60 °C for 24 h. Yield: 83%. Mp. 134-136 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ = 2.98 (s, 6H), 3.71 (s, 3H), 6.39 (s, 1H), 6.79 (d, *J* = 1.2 Hz, 1H), 7.02 (d, *J* = 1.2 Hz, 1H), 7.02-7.14 (m, 1H), 7.28-7.32 (m, 1H), 7.54-7.56 (m, 1H), 7.77-7.79 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C): δ = 33.1, 36.7, 36.8, 44.2, 121.1, 123.4, 127.9, 128.0, 129.3, 131.4, 132.8, 137.4, 146.3, 166.5. HRMS: Calcd for C<sub>14</sub>H<sub>17</sub>BrN<sub>3</sub>OS ([M+H]<sup>+</sup>): 354.0270 and 356.0250, found: 354.0277 and 356.0255.

**S-(3-bromophenyl)(1-methyl-1*H*-imidazol-2-yl)methyl dimethylcarbamothioate (3m)**



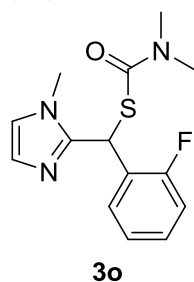
**3m** was obtained as white powder from the reaction of **1** with 3-bromobenzaldehyde at 30 °C for 12 h. Yield: 91%. Mp. 144-146 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ = 2.98 (s, 3H), 2.99 (s, 3H), 3.60 (s, 3H), 5.94 (s, 3H), 6.81 (d, *J* = 1.2 Hz, 1H), 7.03 (d, *J* = 0.8 Hz, 1H), 7.18 (t, *J* = 8.0 Hz, 1H), 7.36-7.39 (m, 1H), 7.42-7.44 (m, 1H), 7.64 (t, *J* = 1.6 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C): δ = 33.0, 36.6, 36.9, 44.3, 121.2, 122.6, 127.2, 127.9, 130.2, 130.8, 131.4, 141.5, 145.8, 166.6. HRMS: Calcd for C<sub>14</sub>H<sub>17</sub>BrN<sub>3</sub>OS ([M+Na]<sup>+</sup>): 376.0090 and 378.0069, found: 376.0098 and 378.0075.

***S*-(3-bromophenyl)(1-methyl-1*H*-imidazol-2-yl)methyl dimethylcarbamothioate (3n)**



**3n** was obtained as white powder from the reaction of **1** with 4-bromobenzaldehyde at 30 °C for 12 h. Yield: 90%. Mp. 96-98 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ = 2.98 (d, *J* = 4.8 Hz, 6H), 3.58 (s, 3H), 5.93 (s, 3H), 6.80 (d, *J* = 1.2 Hz, 1H), 7.02 (d, *J* = 1.2 Hz, 1H), 7.37-7.44 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C): δ = 32.9, 36.6, 36.8, 44.3, 121.2, 121.7, 127.9, 130.2, 131.8, 138.4, 145.9, 166.7. HRMS: Calcd for C<sub>14</sub>H<sub>17</sub>BrN<sub>3</sub>OS ([M+H]<sup>+</sup>): 354.0270 and 356.0250, found: 354.0281 and 356.0258.

***S*-(2-fluorophenyl)(1-methyl-1*H*-imidazol-2-yl)methyl dimethylcarbamothioate (3o)**

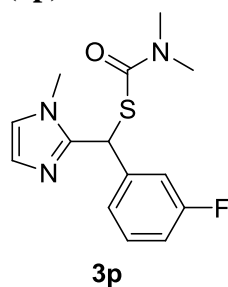


**3o** was obtained as white powder from the reaction of **1** with 2-fluorobenzaldehyde at 30 °C for 12 h. Yield: 88%. Mp. 116-117 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ



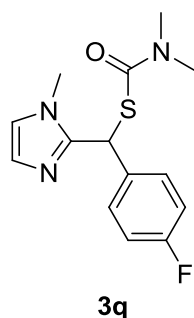
= 2.97 (s, 6H), 3.68 (s, 3H), 6.29 (s, 1H), 6.75 (d,  $J = 0.8$  Hz, 1H), 6.98 (d,  $J = 0.8$  Hz, 1H), 7.01-7.06 (m, 1H), 7.10-7.14 (m, 1H), 7.20-7.26 (m, 1H), 7.68-7.72 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 32.8, 36.6, 36.8, 37.2, 37.3, 115.2, 115.4, 121.0, 124.5, 124.6, 125.8, 125.9, 127.9, 129.3, 129.4, 130.9, 130.9, 146.1, 159.3$  ( $^1J_{\text{CF}} = 245$  Hz), 166.5. HRMS: Calcd for  $\text{C}_{14}\text{H}_{17}\text{FN}_3\text{OS}$  ( $[\text{M}+\text{H}]^+$ ): 294.1071, found: 294.1080.

***S*-(3-fluorophenyl)(1-methyl-1*H*-imidazol-2-yl)methyl dimethylcarbamothioate (3p)**



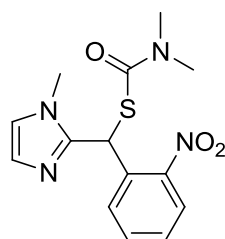
**3p** was obtained as white powder from the reaction of **1** with 3-fluorobenzaldehyde at 30 °C for 12 h. Yield: 89%. Mp. 89-91 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 2.99$  (s, 6H), 3.60 (s, 3H), 5.97 (s, 1H), 6.81 (d,  $J = 2.0$  Hz, 1H), 6.91-6.96 (m, 1H), 7.03-7.04 (m, 1H), 7.21-7.28 (m, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 33.0, 36.7, 36.9, 44.3, 44.4, 114.6, 114.8, 115.4, 115.6, 121.2, 124.0, 124.1, 127.8, 130.1, 130.2, 141.7, 141.7, 146.0, 162.8$  ( $^1J_{\text{CF}} = 245$  Hz), 166.7. HRMS: Calcd for  $\text{C}_{14}\text{H}_{17}\text{FN}_3\text{OS}$  ( $[\text{M}+\text{H}]^+$ ): 294.1071, found: 294.1081.

***S*-(4-fluorophenyl)(1-methyl-1*H*-imidazol-2-yl)methyl dimethylcarbamothioate (3q)**



**3q** was obtained as white powder from the reaction of **1** with 4-fluorobenzaldehyde at 30 °C for 12 h. Yield: 85%. Mp. 111-113 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 2.98$  (s, 6H), 3.59 (s, 3H), 5.95 (s, 1H), 6.80 (s, 1H), 6.97-7.02 (m, 3H), 7.46-7.49 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 32.9, 36.6, 36.8, 44.1, 115.4, 115.6, 121.1, 127.8, 130.1, 130.2, 135.1, 146.3, 162.2$  ( $^1J_{\text{CF}} = 246$  Hz), 166.8. HRMS: Calcd for  $\text{C}_{14}\text{H}_{17}\text{FN}_3\text{OS}$  ( $[\text{M}+\text{H}]^+$ ): 294.1071, found: 294.1080.

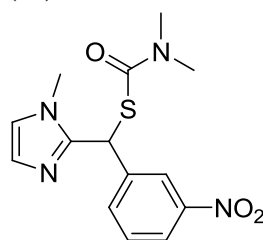
***S*-(1-methyl-1*H*-imidazol-2-yl)(2-nitrophenyl)methyl dimethylcarbamothioate (3r)**



**3r**

**3r** was obtained as white powder from the reaction of **1** with 2-nitrobenzaldehyde at 60 °C for 24 h. Yield: 89%. Mp. 161-164 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 2.95 (s, 6H), 3.80 (s, 3H), 6.74 (s, 1H), 6.85 (d,  $J$  = 0.8 Hz, 1H), 6.99 (d,  $J$  = 0.8 Hz, 1H), 7.39-7.43 (m, 1H), 7.63-7.67 (m, 1H), 7.90-7.92 (m, 1H), 8.18-8.20 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 31.7, 33.2, 36.6, 36.9, 40.0, 121.6, 124.4, 128.0, 128.3, 132.6, 133.3, 134.2, 144.7, 148.3, 165.8. HRMS: Calcd for C<sub>14</sub>H<sub>16</sub>N<sub>4</sub>O<sub>3</sub>SNa ([M+Na]<sup>+</sup>): 343.0835, found: 343.0846.

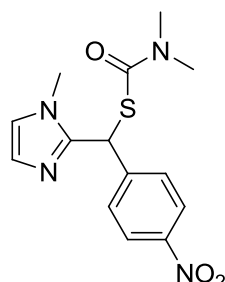
**S-(1-methyl-1H-imidazol-2-yl)(3-nitrophenyl)methyl dimethylcarbamothioate (3s)**



**3s**

**3s** was obtained as white powder from the reaction of **1** with 3-nitrobenzaldehyde at 30 °C for 12 h. Yield: 98%. Mp. 72-75 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 3.00 (d,  $J$  = 6.8 Hz, 6H), 3.68 (s, 3H), 6.09 (s, 1H), 6.86 (d,  $J$  = 1.2 Hz, 6H), 7.02 (d,  $J$  = 1.2 Hz, 6H), 7.48-7.52 (m, 1H), 7.90-7.92 (m, 1H), 8.09-8.12 (m, 1H), 8.42-8.43 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 33.0, 36.6, 36.9, 44.1, 121.6, 122.6, 123.6, 128.2, 129.4, 134.9, 141.7, 144.9, 148.2, 166.0. HRMS: Calcd for C<sub>14</sub>H<sub>17</sub>N<sub>4</sub>O<sub>3</sub>S ([M+H]<sup>+</sup>): 321.1016, found: 321.1014.

**S-(1-methyl-1H-imidazol-2-yl)(4-nitrophenyl)methyl dimethylcarbamothioate (3t)**

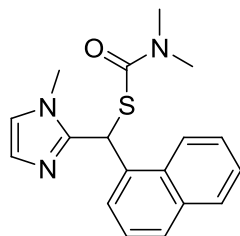


**3t**

**3t** was obtained as white powder from the reaction of **1** with 4-nitrobenzaldehyde at 30 °C for 12 h. Yield: 86%. Mp. 138-139 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  =

2.99 (d,  $J = 10.0$  Hz, 6H), 3.64 (s, 3H), 6.06 (s, 1H), 6.85 (s, 1H), 7.04 (s, 1H), 7.72 (d,  $J = 8.8$  Hz, 2H), 8.15-8.18 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 33.0$ , 36.6, 37.0, 44.1, 121.6, 123.8, 128.2, 129.6, 144.8, 146.9, 147.2, 166.1. HRMS: Calcd for  $\text{C}_{14}\text{H}_{17}\text{N}_4\text{O}_3\text{S}$  ( $[\text{M}+\text{H}]^+$ ): 321.1016, found: 321.1013.

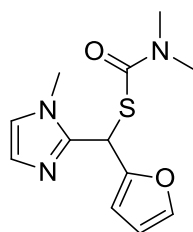
***S*-(1-methyl-1*H*-imidazol-2-yl)(naphthalen-1-yl)methyl dimethylcarbamothioate (3u)**



**3u**

**3u** was obtained as white powder from the reaction of **1** with 1-naphthaldehyde at 30 °C for 12 h. Yield: 81%. Mp. 196-198 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 2.96$  (s, 3H), 3.01 (s, 3H), 3.47 (s, 3H), 6.72 (s, 1H), 6.81 (d,  $J = 6.0$  Hz, 1H), 7.09 (d,  $J = 5.7$  Hz, 1H), 7.35-7.39 (m, 1H), 7.49-7.54 (m, 2H), 7.58-7.62 (m, 1H), 7.76-7.78 (m, 1H), 7.86-7.89 (m, 1H), 8.31 (d,  $J = 8.8$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 32.9$ , 36.7, 36.9, 41.7, 121.4, 123.3, 125.5, 125.9, 126.8, 127.6, 128.8, 129.0, 130.5, 133.3, 134.1, 147.0, 167.2. HRMS: Calcd for  $\text{C}_{18}\text{H}_{20}\text{N}_3\text{OS}$  ( $[\text{M}+\text{H}]^+$ ): 326.1322, found: 326.1325.

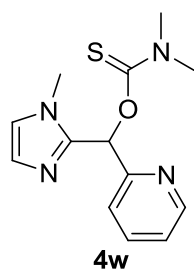
***S*-furan-2-yl(1-methyl-1*H*-imidazol-2-yl)methyl dimethylcarbamothioate (3v)**



**3v**

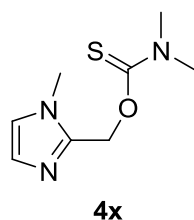
**3v** was obtained as white powder from the reaction of **1** with furan-2-carbaldehyde at 30 °C for 12 h. Yield: 84%. Mp. 89-91 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 2.99$  (s, 3H), 3.01 (s, 3H), 3.68 (d,  $J = 1.2$  Hz, 3H), 6.15 (s, 1H), 6.30-6.33 (m, 2H), 6.81 (s, 1H), 7.03 (s, 1H), 7.27 (s, 1H), 7.38 (d,  $J = 0.8$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 33.0$ , 36.6, 36.9, 38.8, 108.8, 110.6, 121.2, 128.0, 142.7, 144.8, 150.9, 166.5. HRMS: Calcd for  $\text{C}_{12}\text{H}_{16}\text{N}_3\text{O}_2\text{S}$  ( $[\text{M}+\text{H}]^+$ ): 266.0958, found: 266.0962.

***O*-(1-methyl-1*H*-imidazol-2-yl)(pyridin-2-yl)methyl dimethylcarbamothioate (4w)**



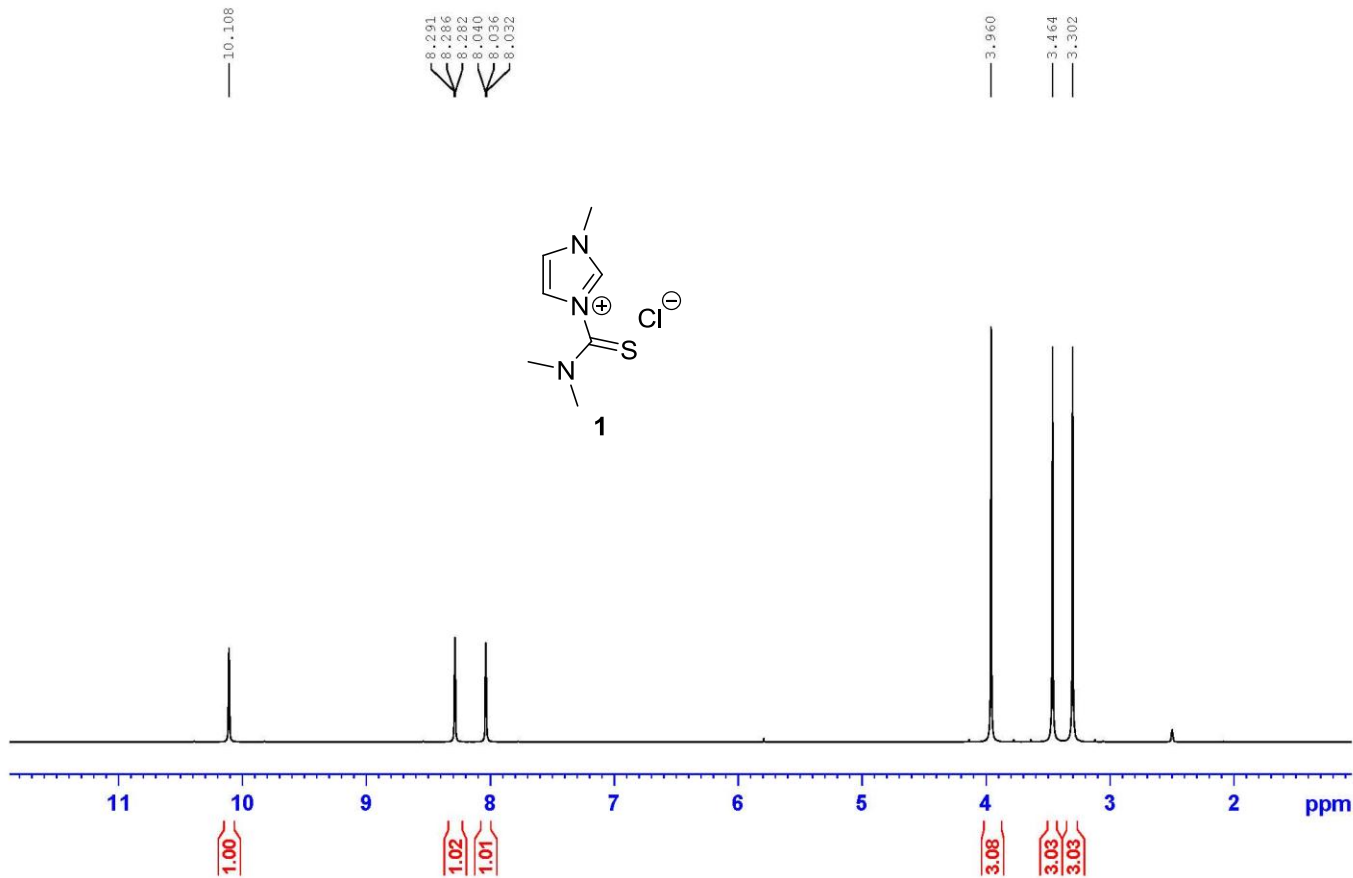
**4w** was obtained as white powder from the reaction of **1** with picolinaldehyde at 30 °C for 12 h. Yield: 85%. Mp. 98-101 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 3.32 (s, 3H), 3.38 (s, 3H), 3.90 (s, 3H), 6.85 (d,  $J$  = 1.2 Hz, 1H), 7.01 (d,  $J$  = 1.2 Hz, 1H), 7.19-7.23 (m, 1H), 7.27 (s, 1H), 7.61-7.64 (m, 1H), 7.66 (d,  $J$  = 5.2 Hz, 1H), 7.71-7.76 (m, 1H), 8.53-8.55 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 33.5, 38.4, 43.2, 75.8, 121.3, 121.5, 122.4, 123.0, 128.3, 137.0, 145.2, 149.2, 157.2, 186.7. HRMS: Calcd for C<sub>13</sub>H<sub>17</sub>N<sub>4</sub>OS ([M+H]<sup>+</sup>): 277.1127, found: 277.1118.

**O-(1-methyl-1H-imidazol-2-yl)methyl dimethylcarbamothioate (4x)**

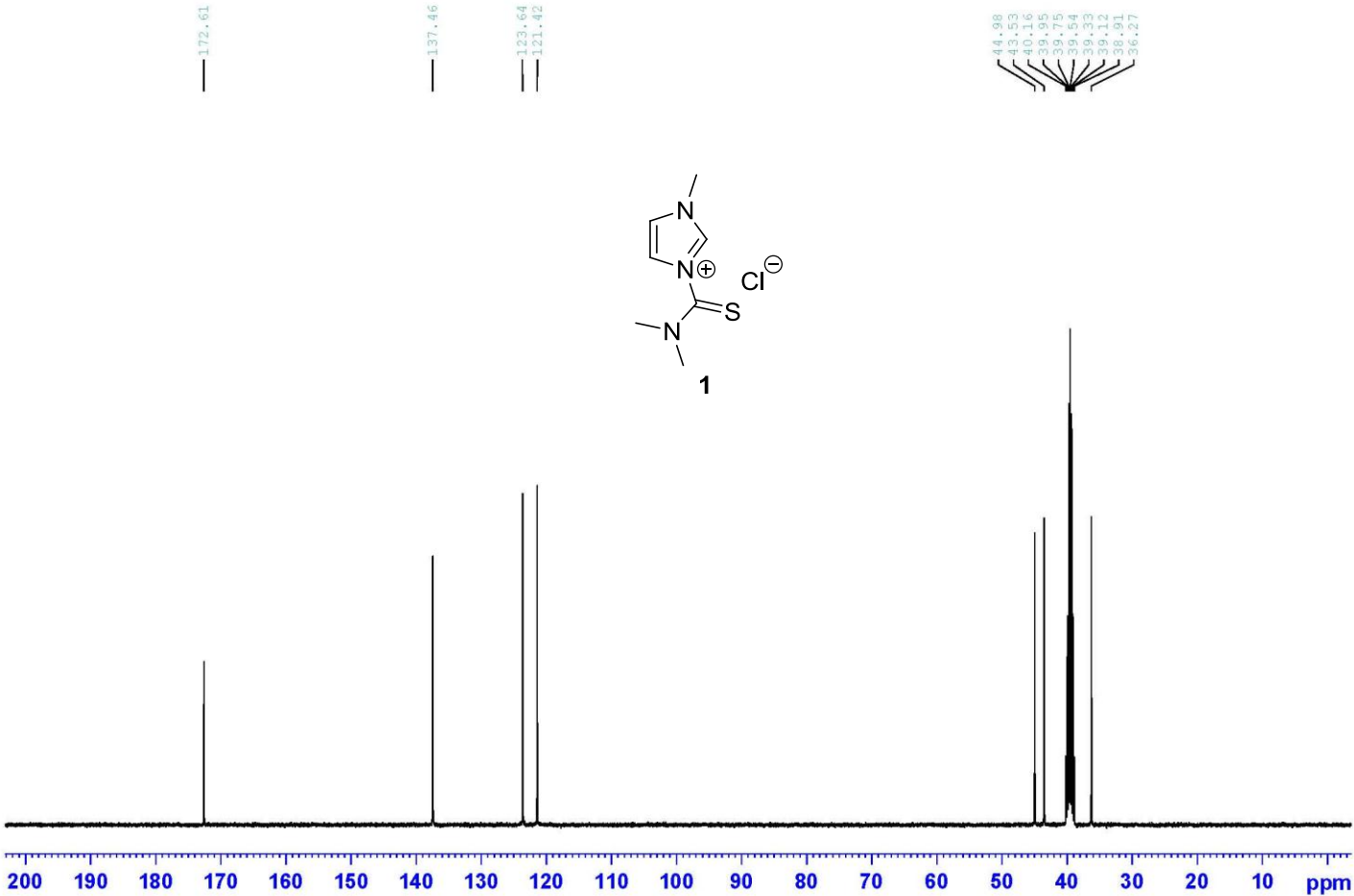


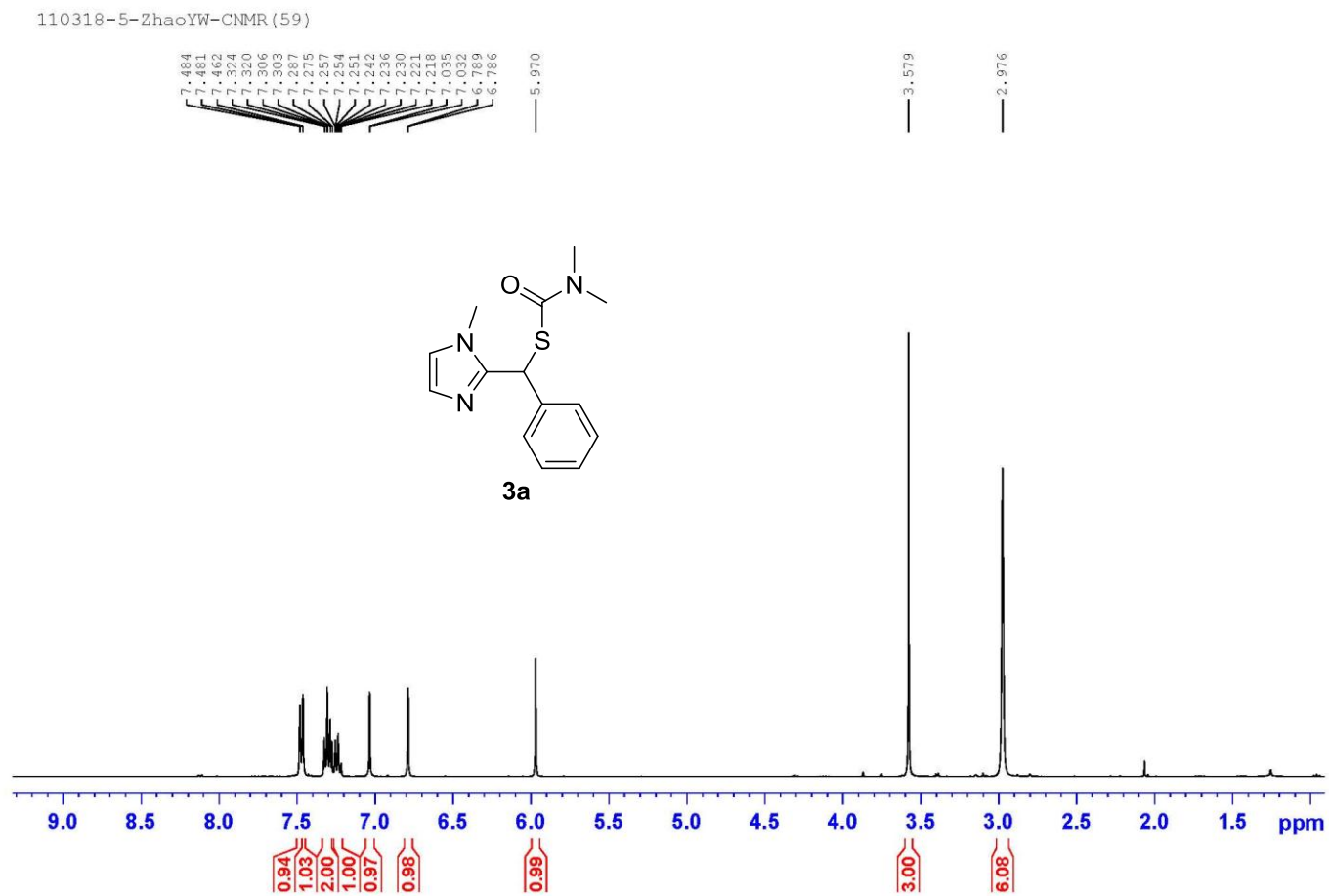
**4x** was obtained as yellow powder from the reaction of **1** with paraformaldehyde at 30 °C for 12 h. Yield: 94%. Mp. 50-52 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 3.11 (s, 3H), 3.38 (s, 3H), 3.71 (s, 3H), 5.57 (s, 1H), 6.92 (d,  $J$  = 1.2 Hz, 1H), 7.03 (d,  $J$  = 1.2 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 33.2, 38.0, 43.0, 64.2, 122.3, 128.3, 142.7, 187.3. HRMS: Calcd for C<sub>8</sub>H<sub>14</sub>N<sub>3</sub>OS ([M+H]<sup>+</sup>): 200.0852, found: 200.0847.

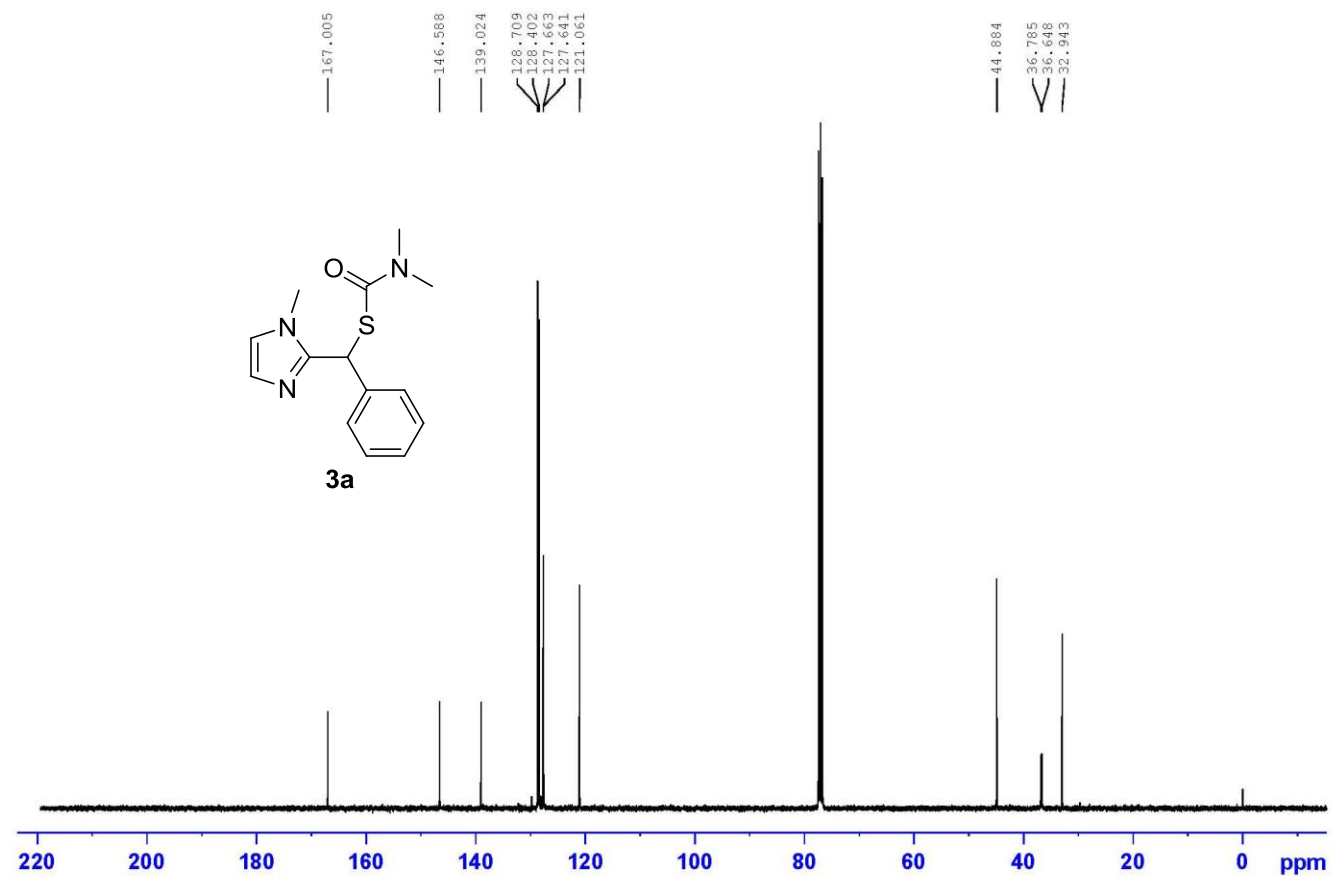
110202-1-ZhaoYW-HNMR (30)



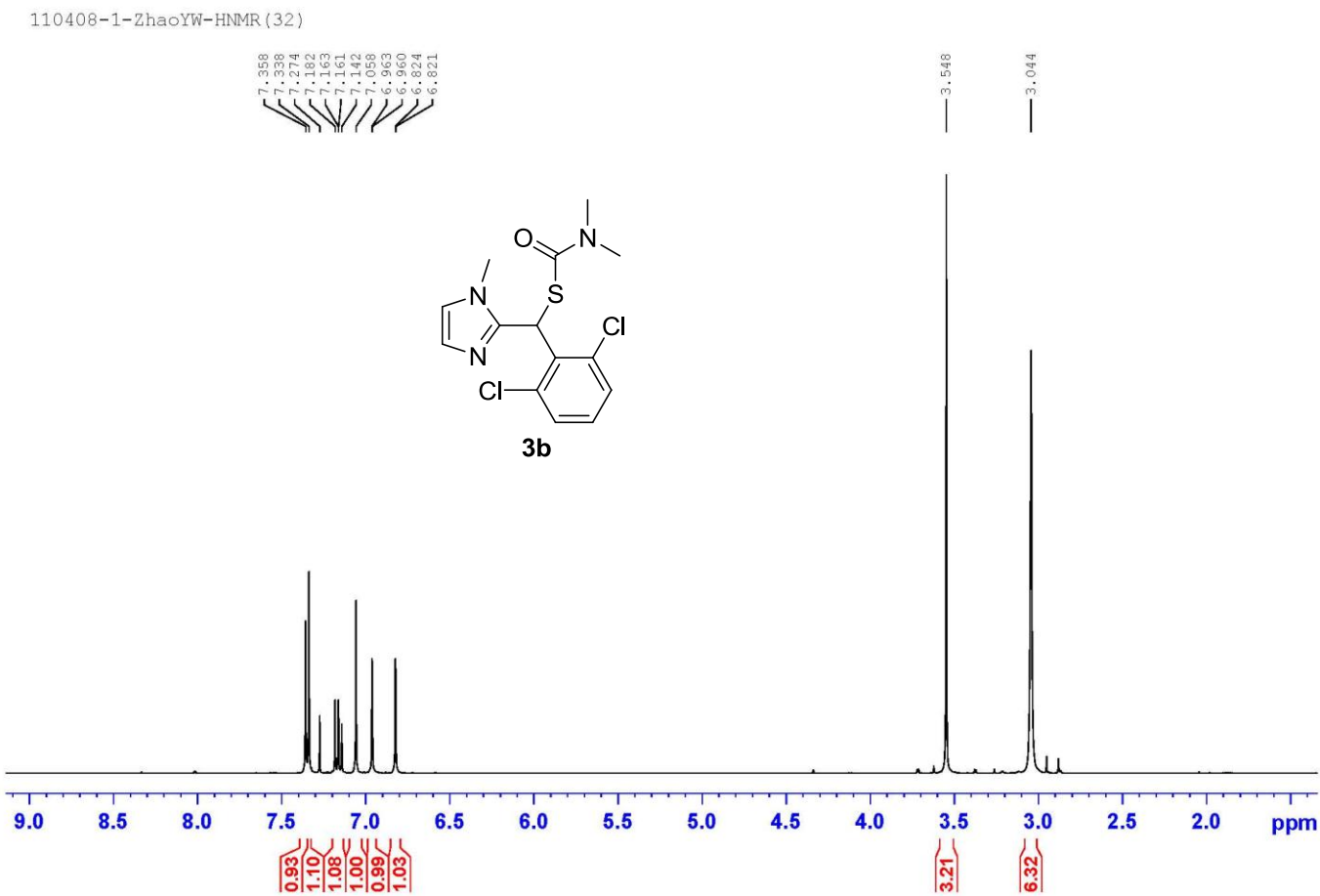
110202-1-ZhaoYW-CNMR (31)



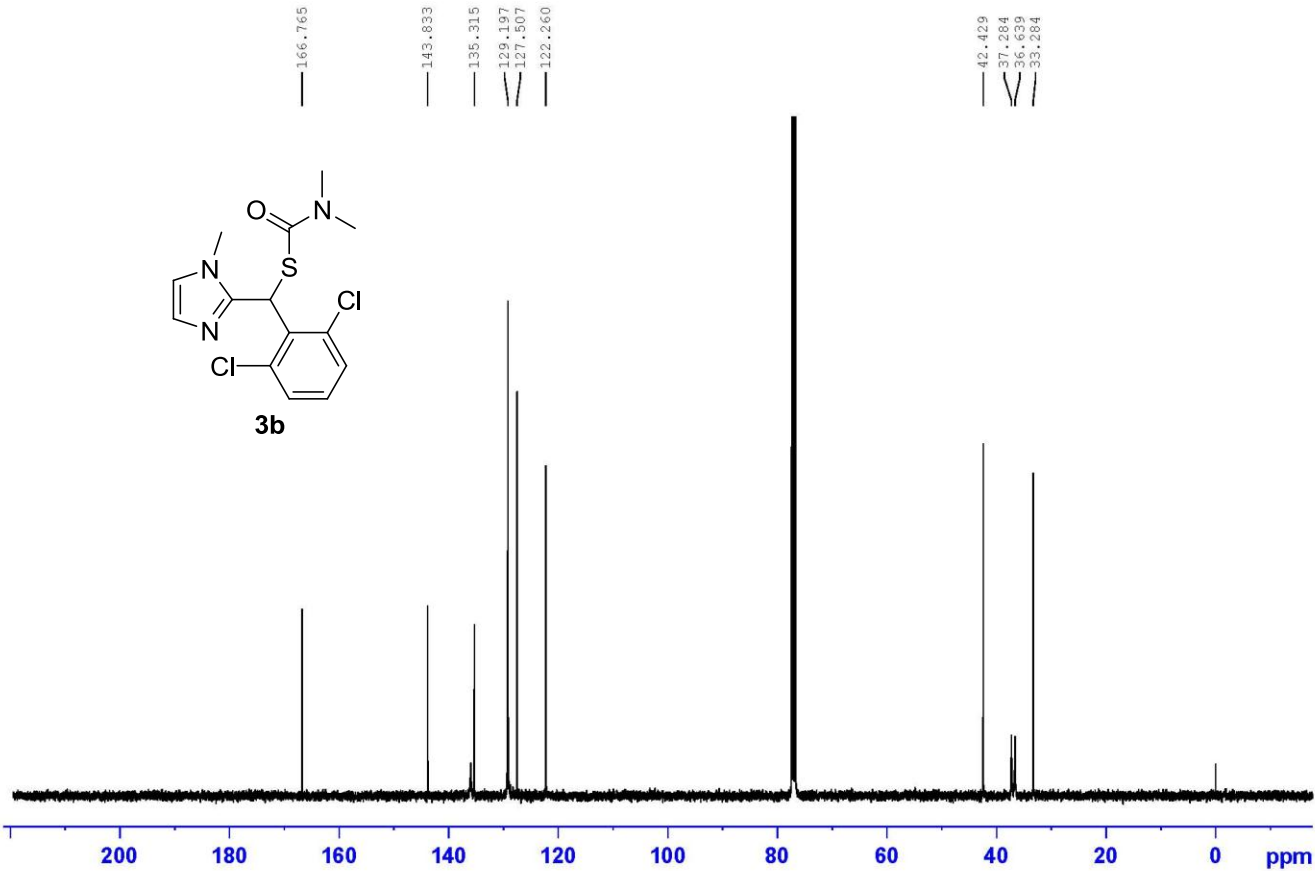


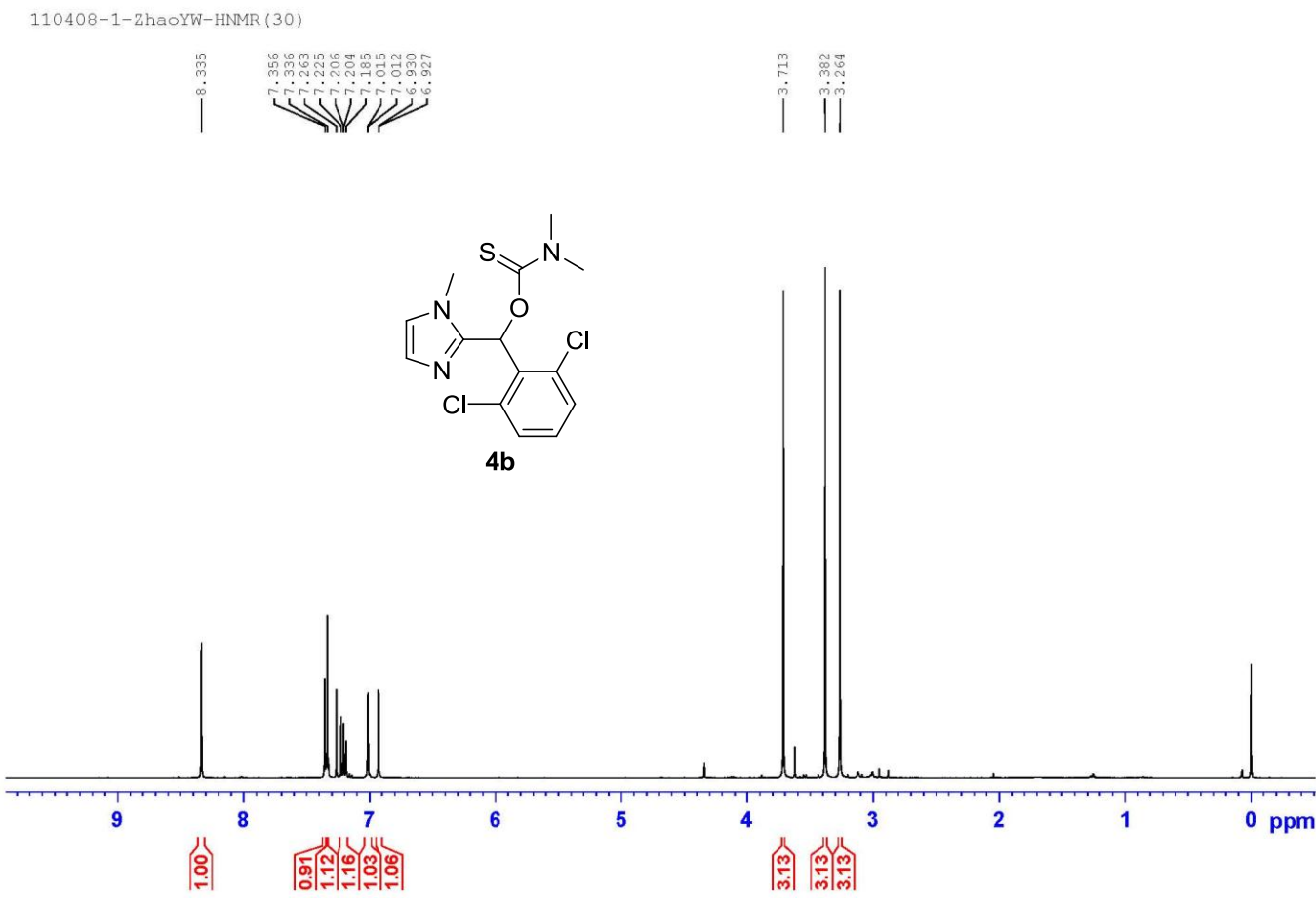




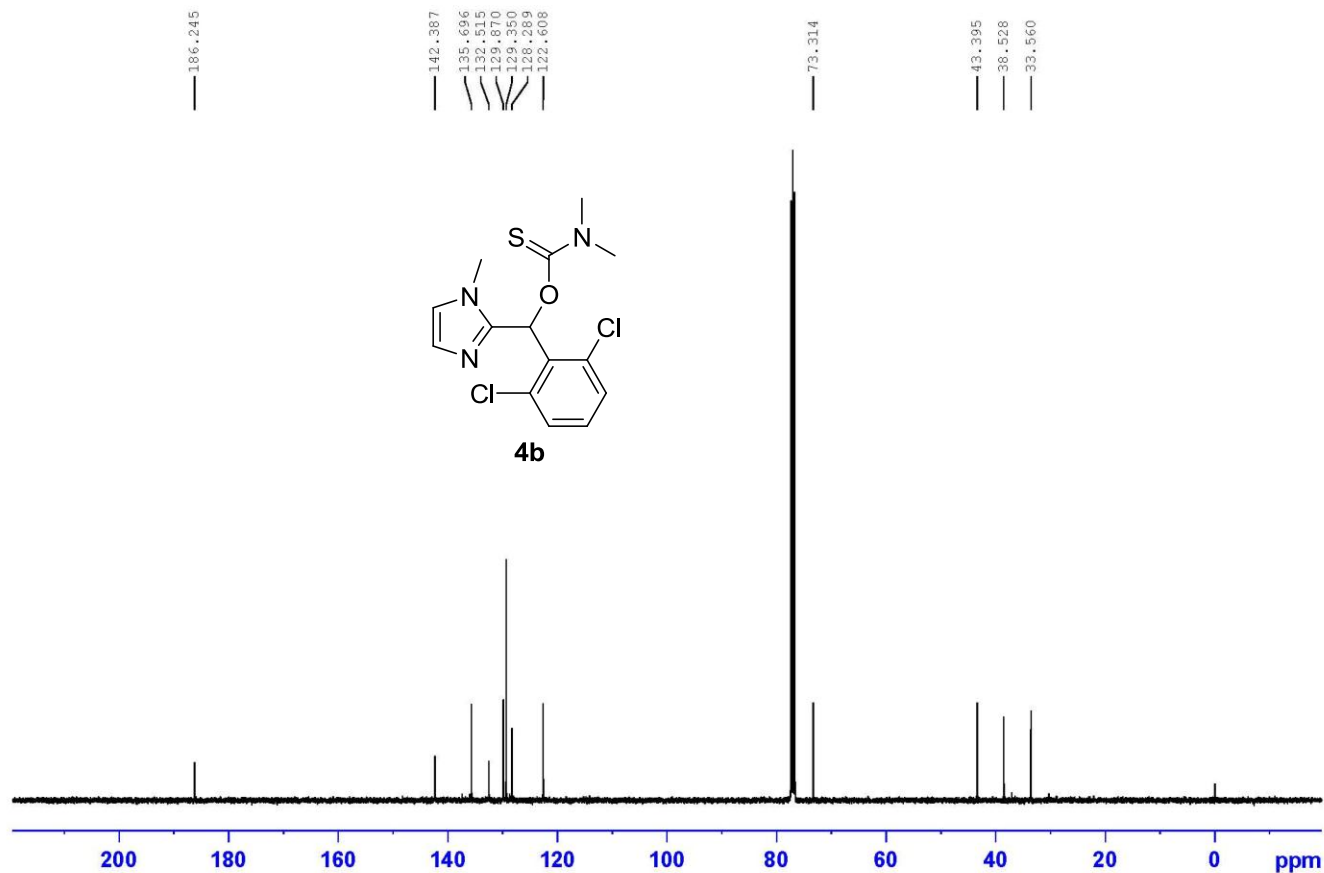


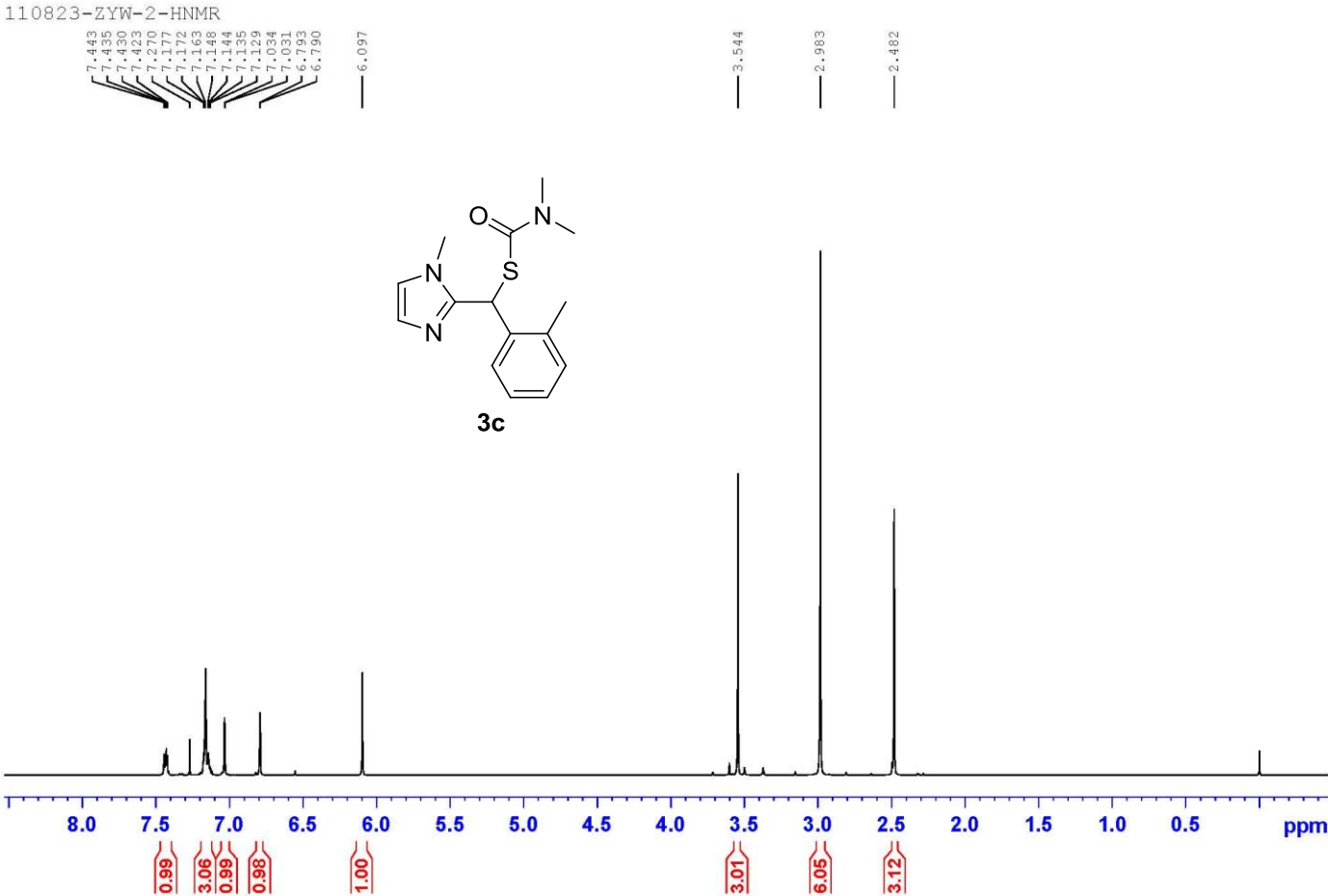
110408-1-ZhaoYW-CNMR (33)



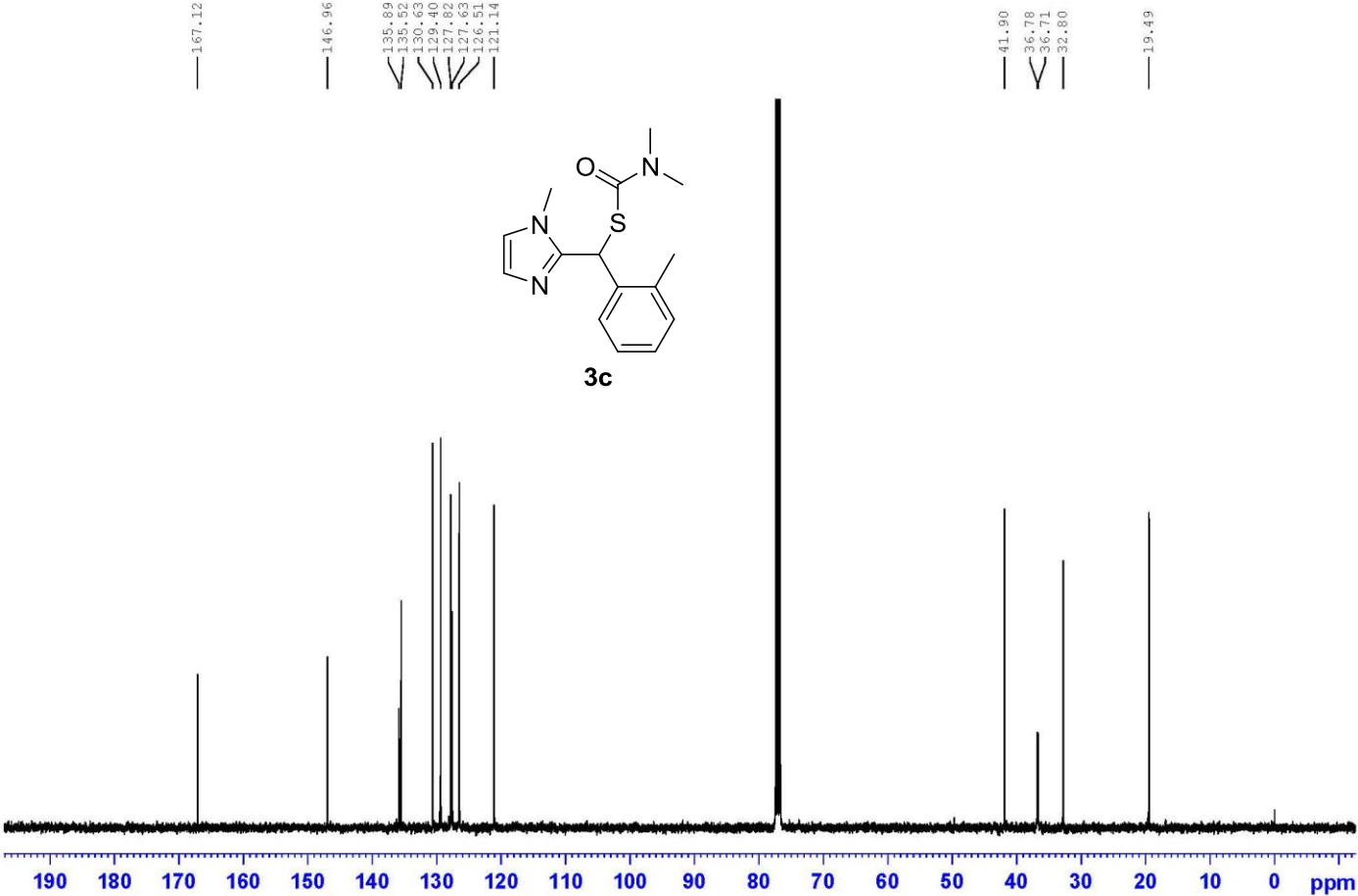


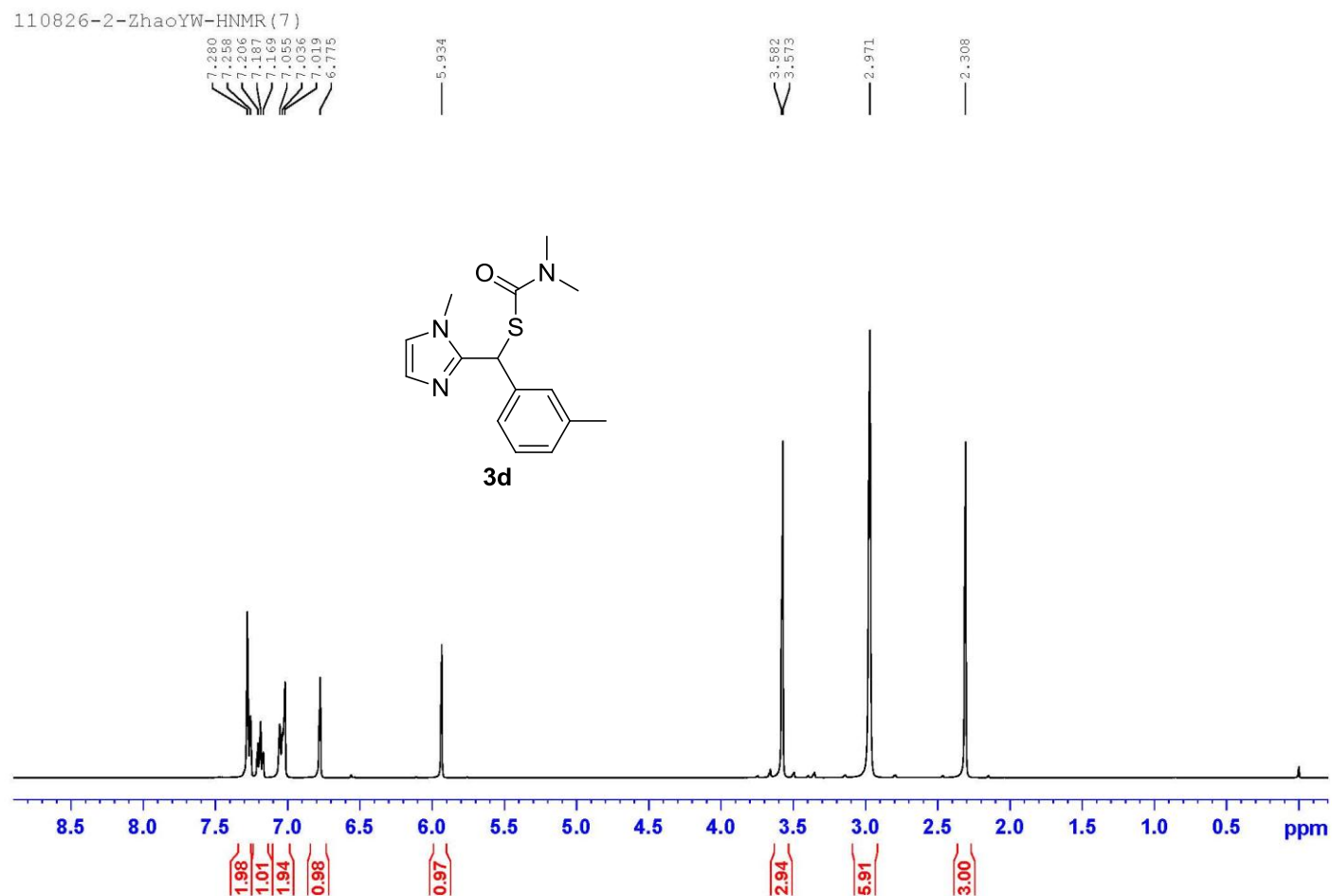
110408-1-ZhaoYW-CNMR (31)



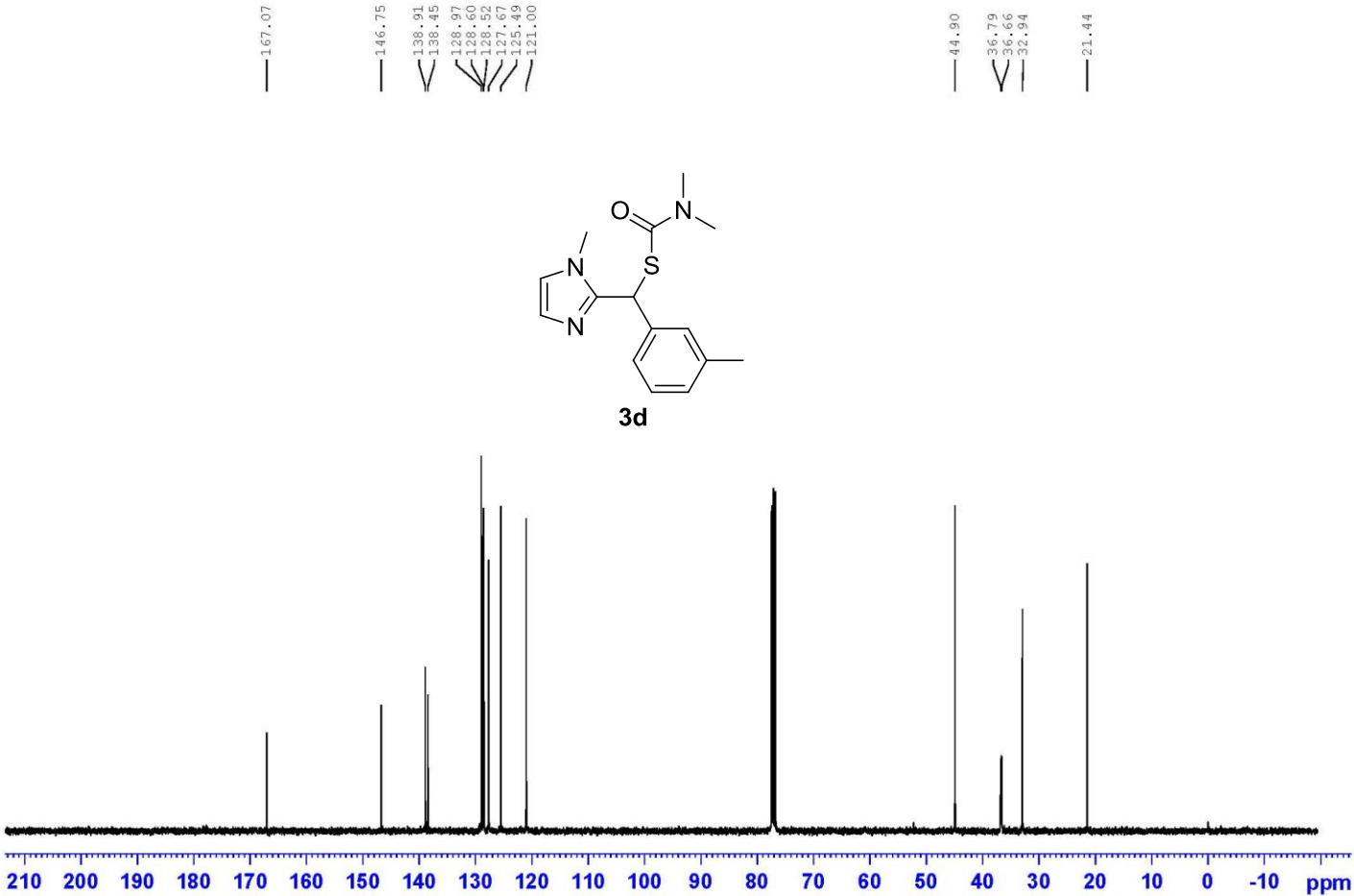


110823-ZYW-2-CNMR



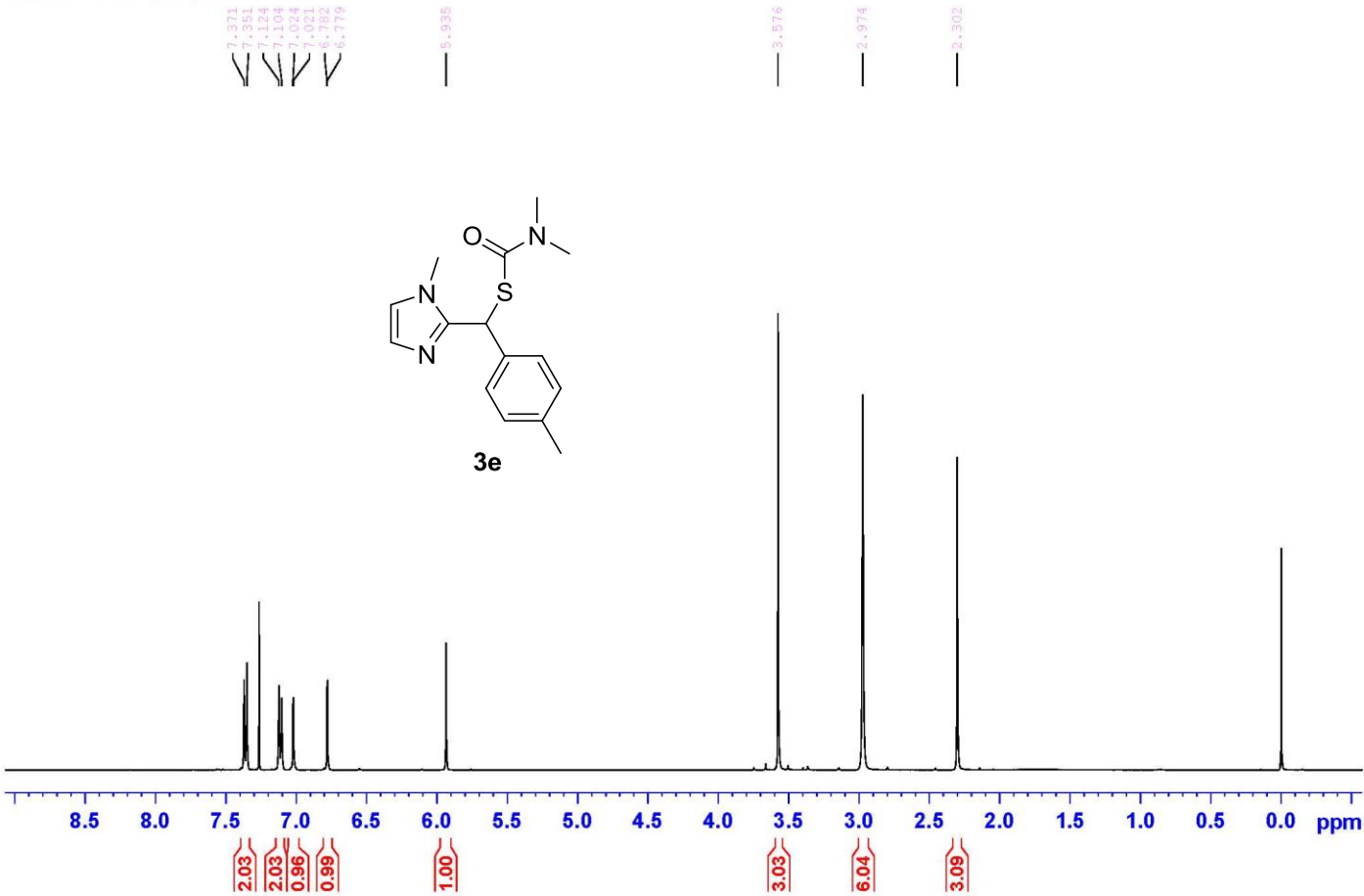


110826-2-ZhaoYW-CNMR (8)

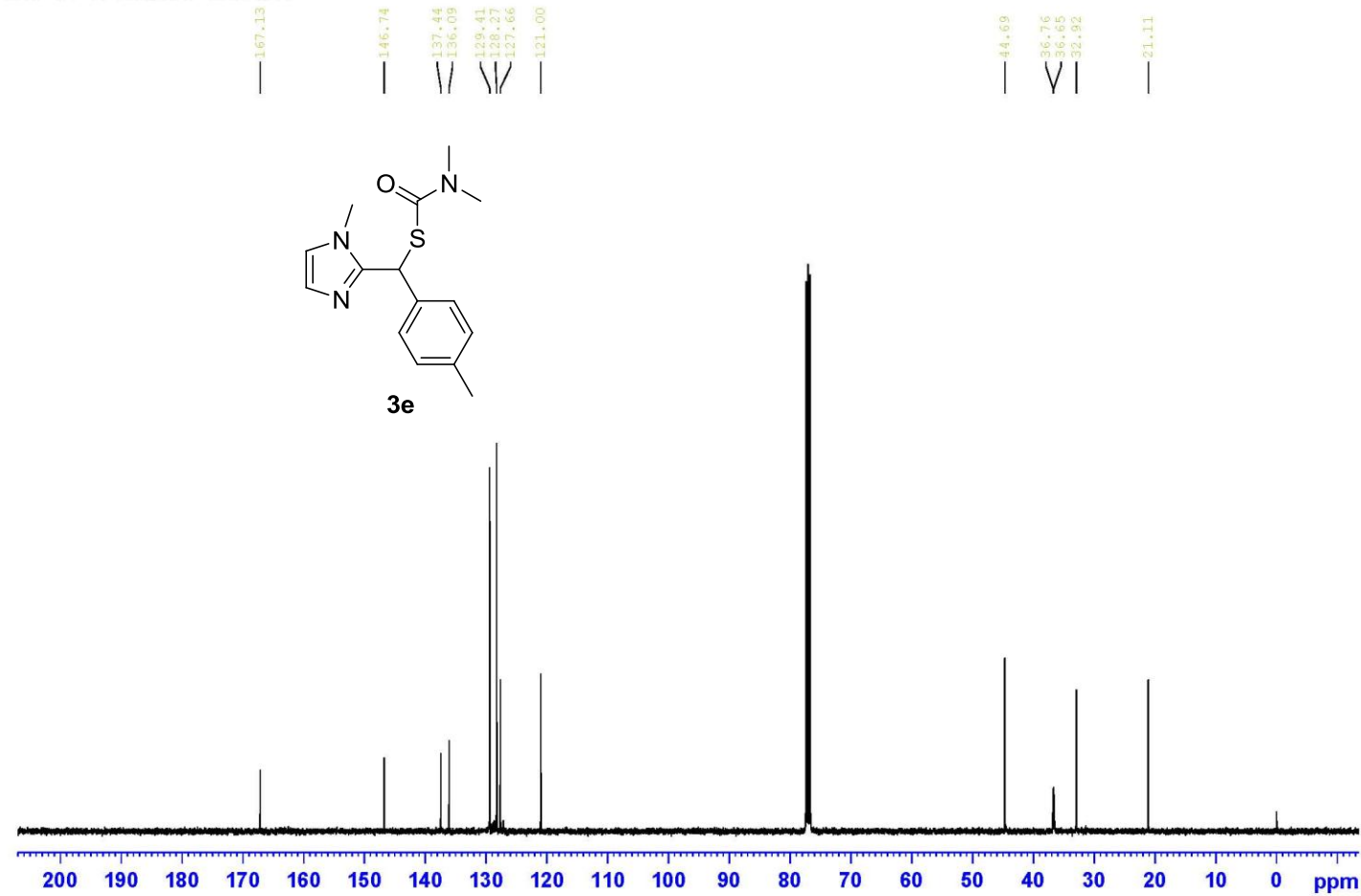


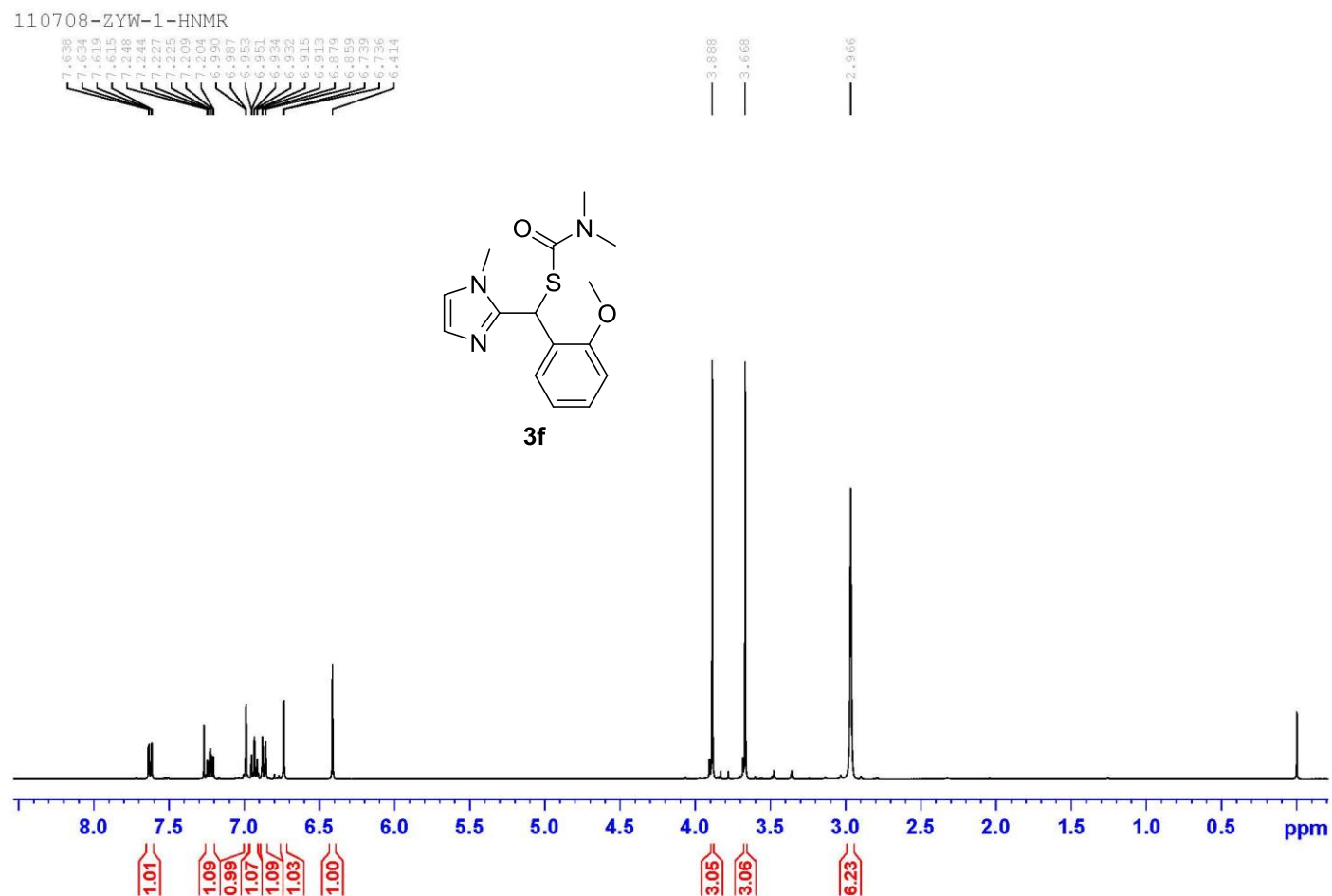


110816-zhaoyingwei-6-HNMR

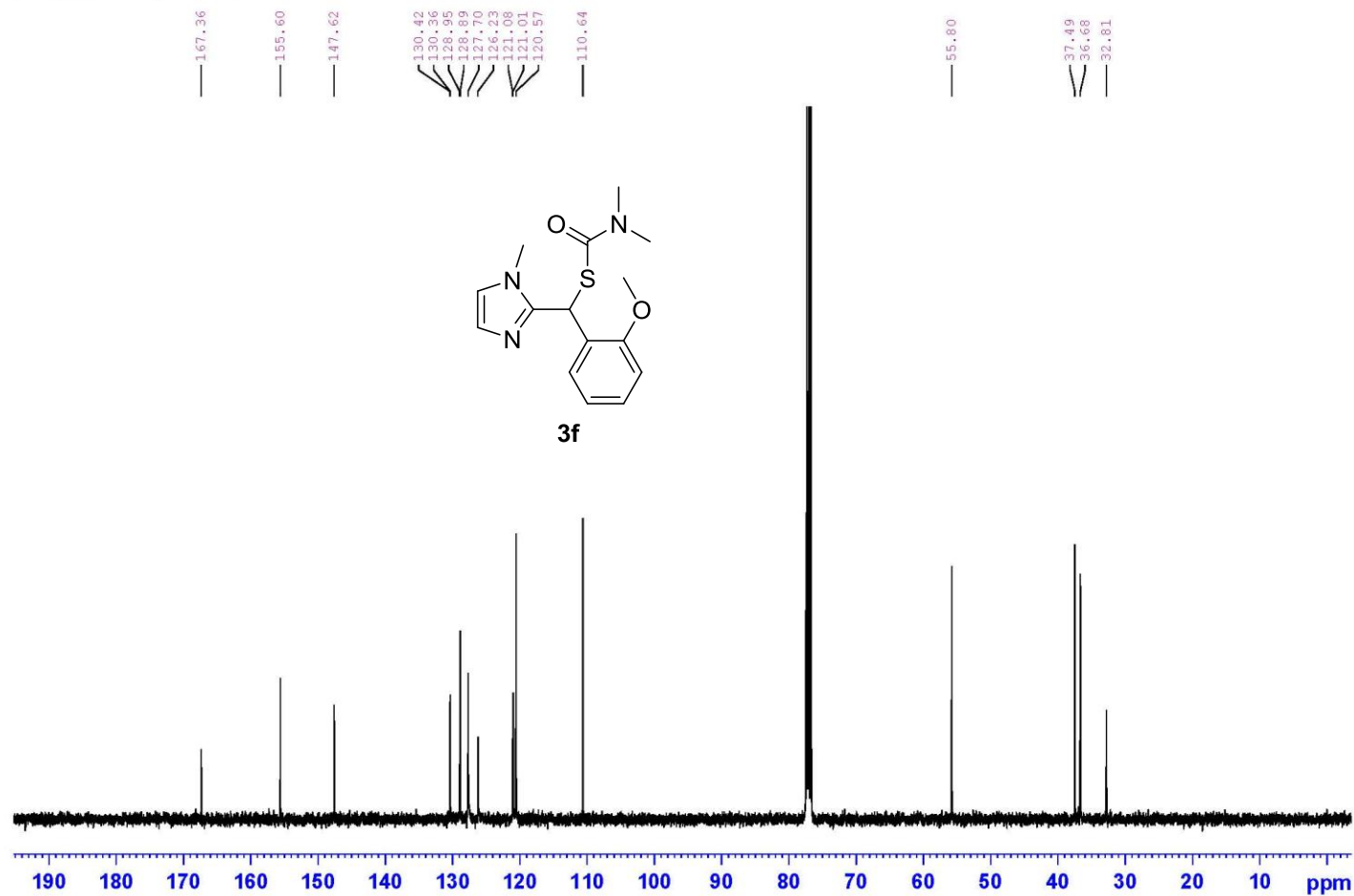


110715-2-ZhaoYW-CNMR (6)

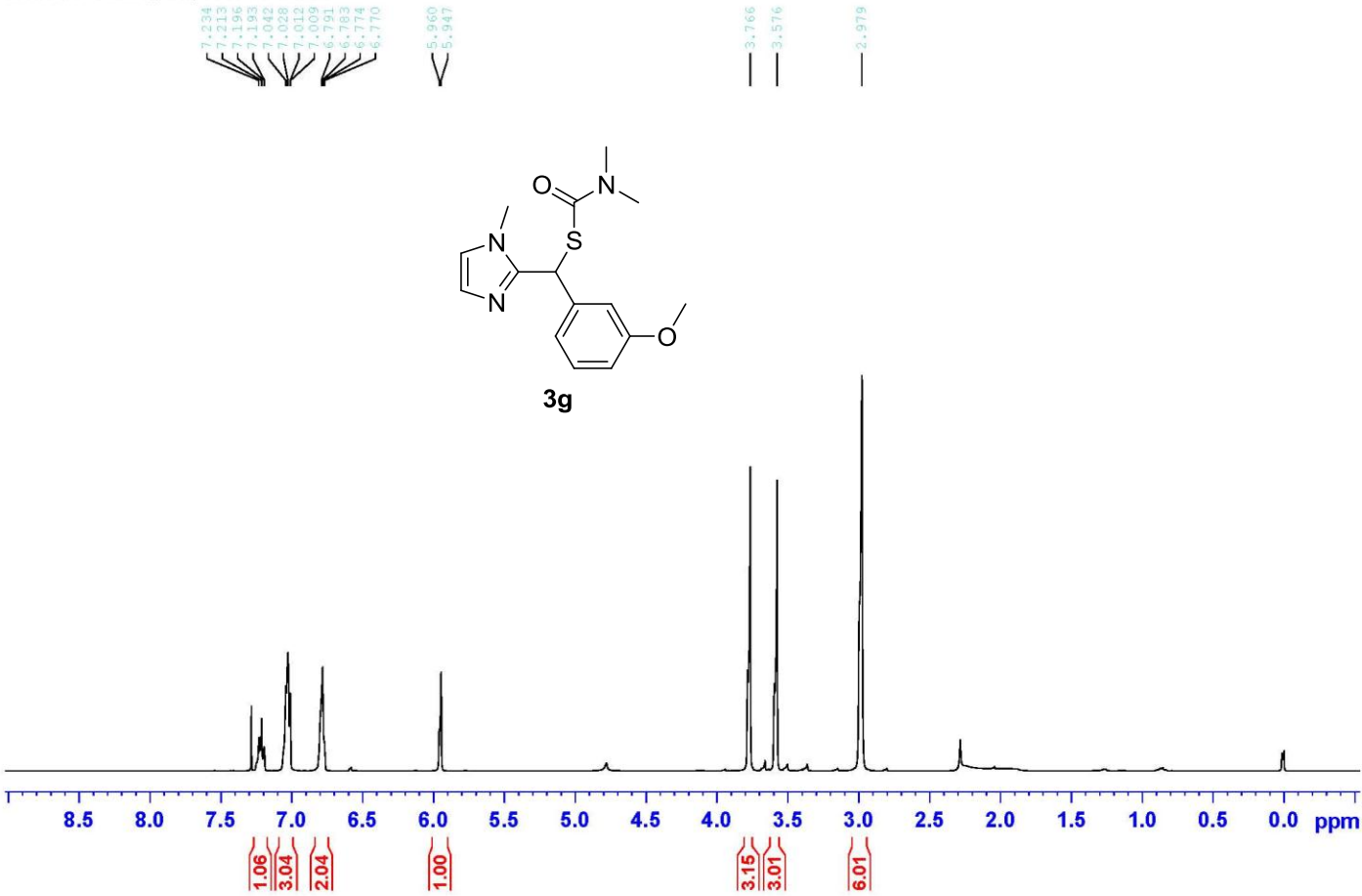




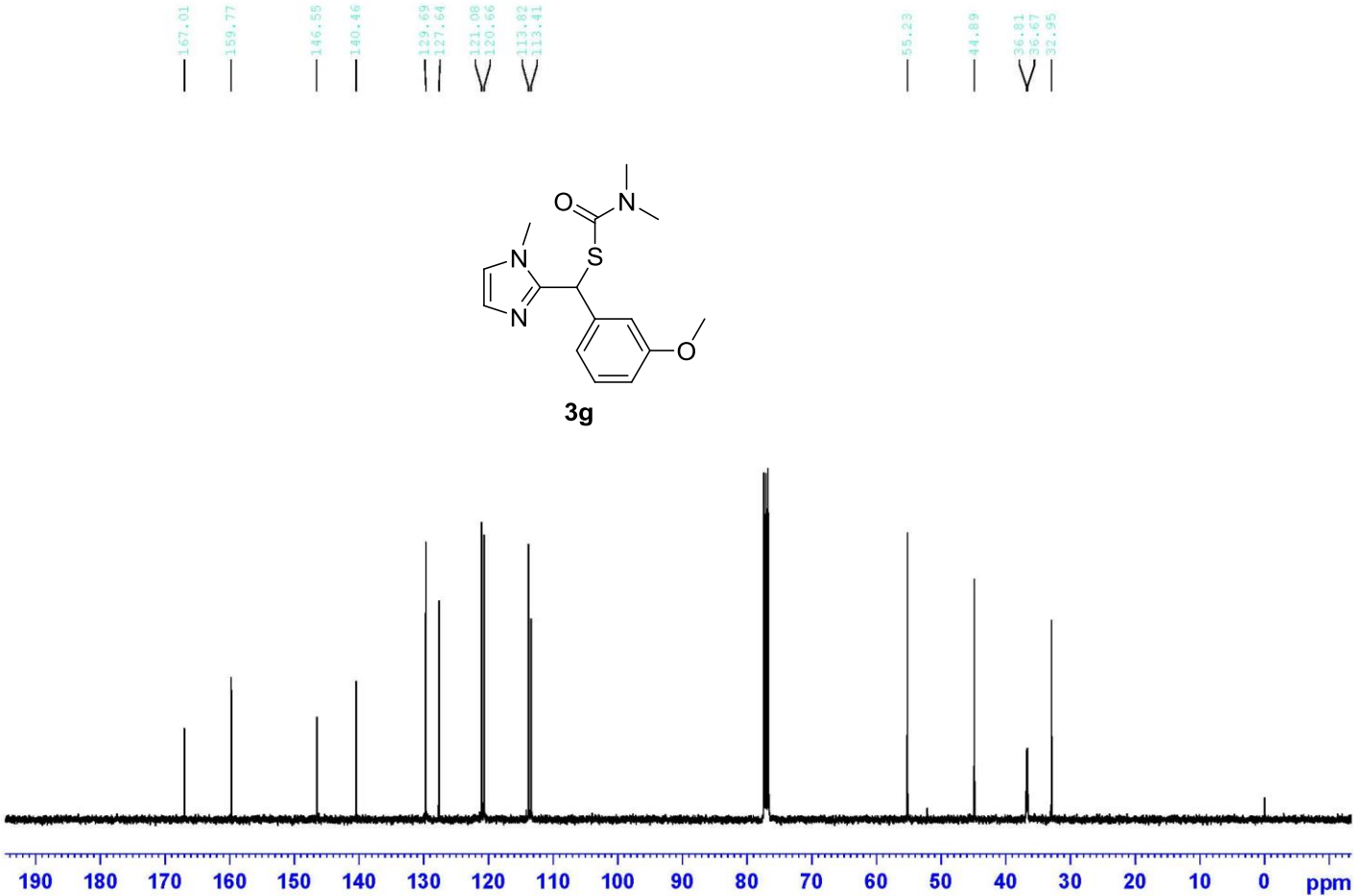
110816-zhaoyingwei-1-CNMR

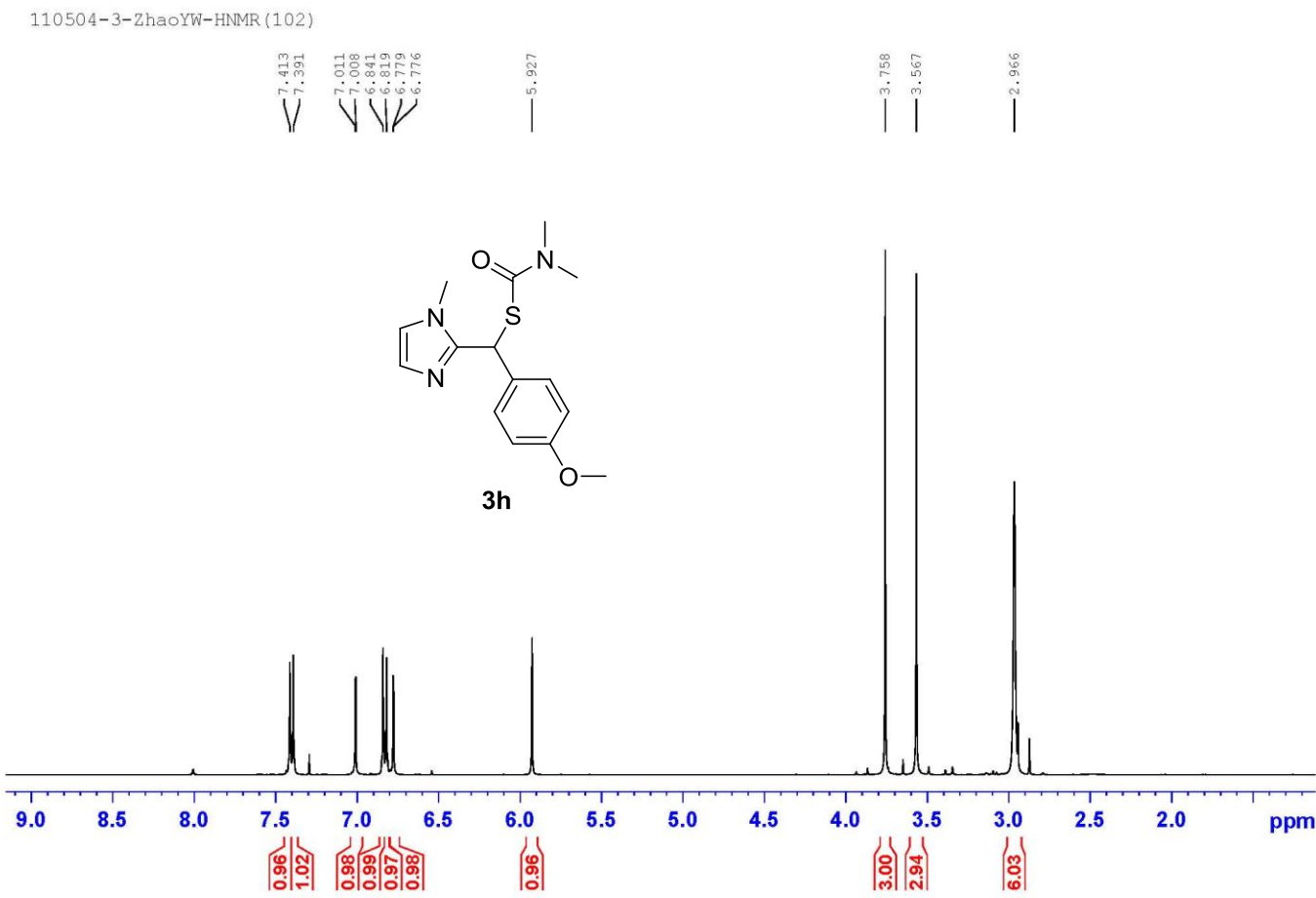


110816-zhaoyingwei-2-HNMR

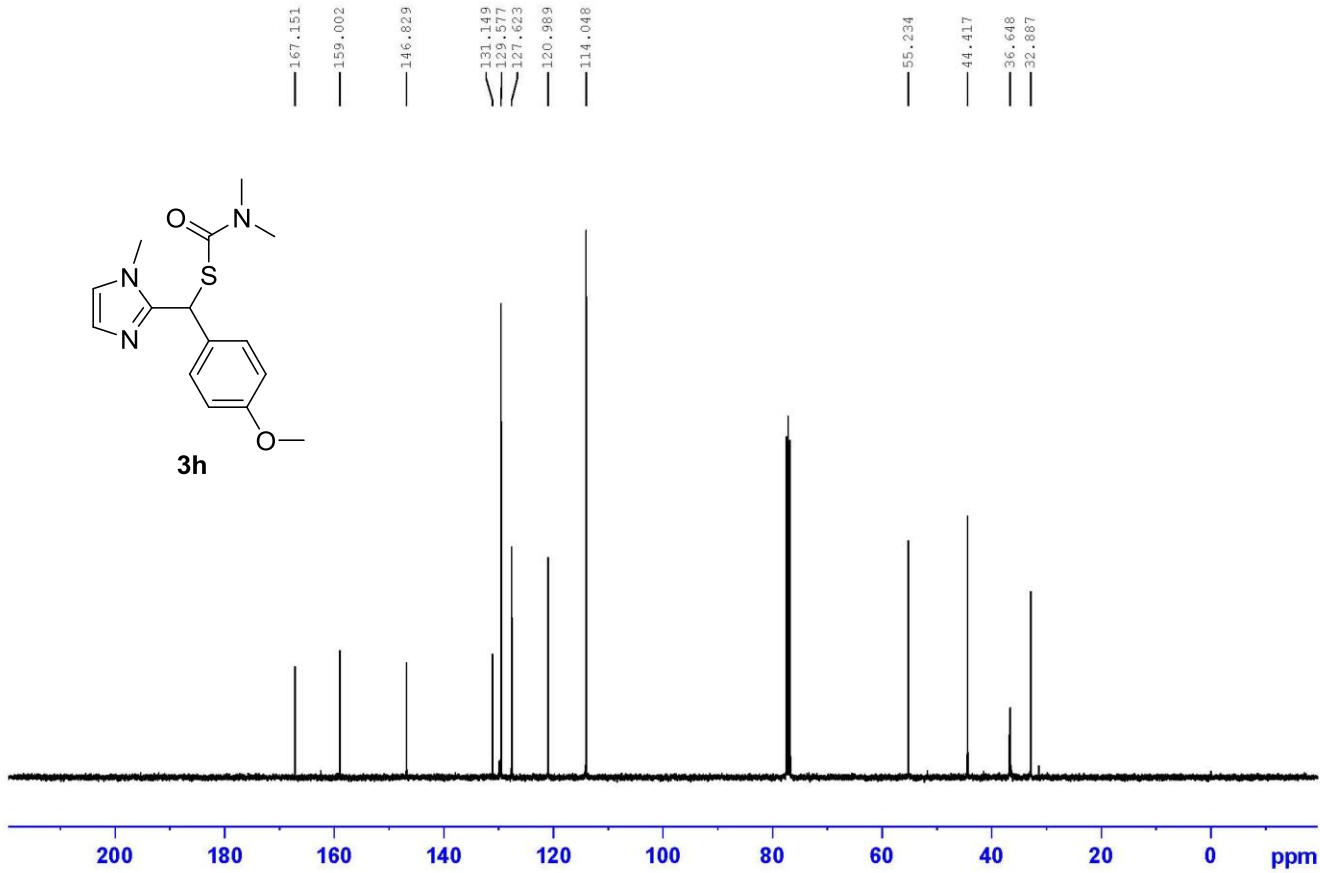


110816-zhaoyingwei-2-CNMR



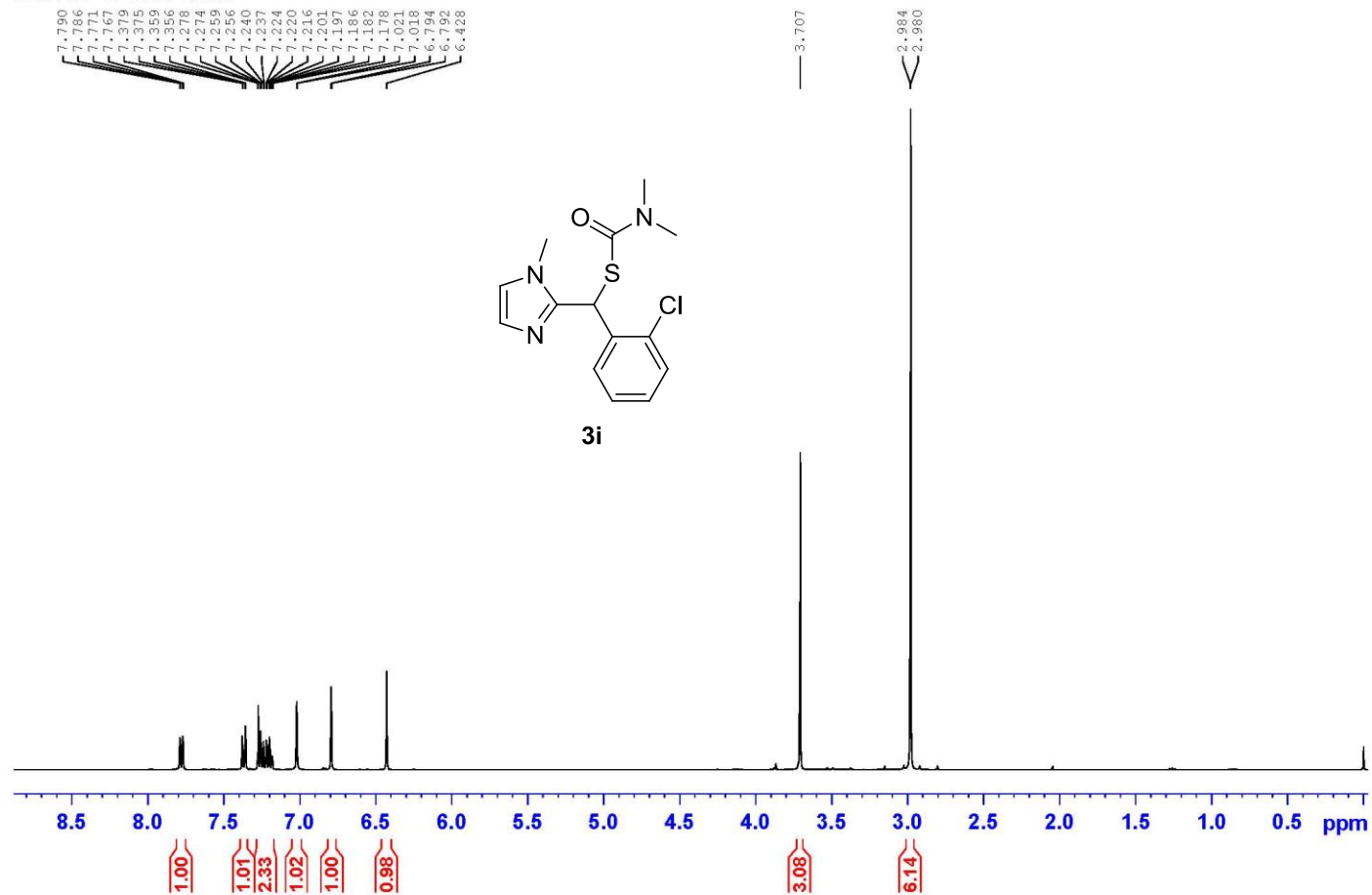


110504-3-ZhaoYW-CNMR (103)

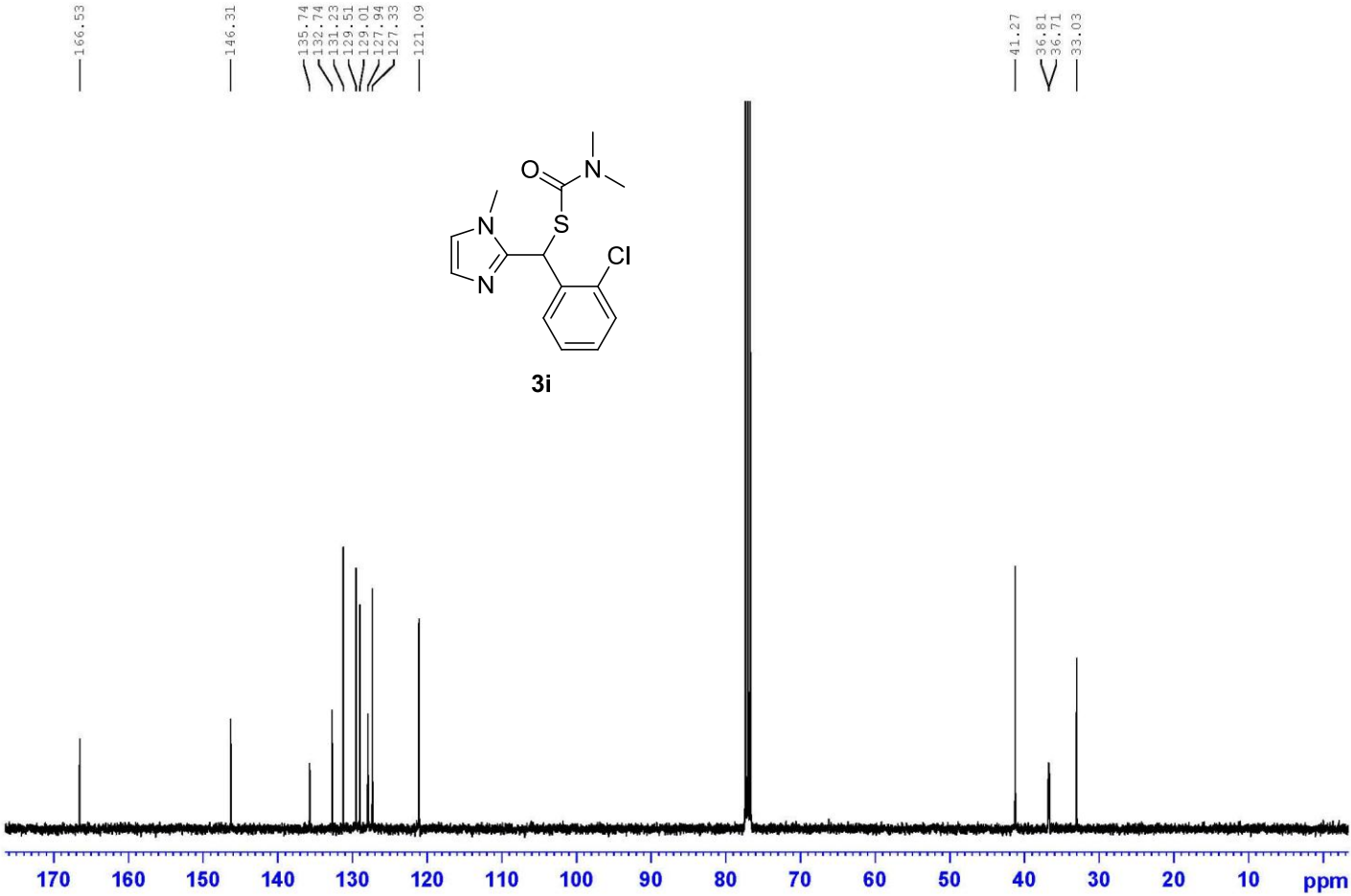


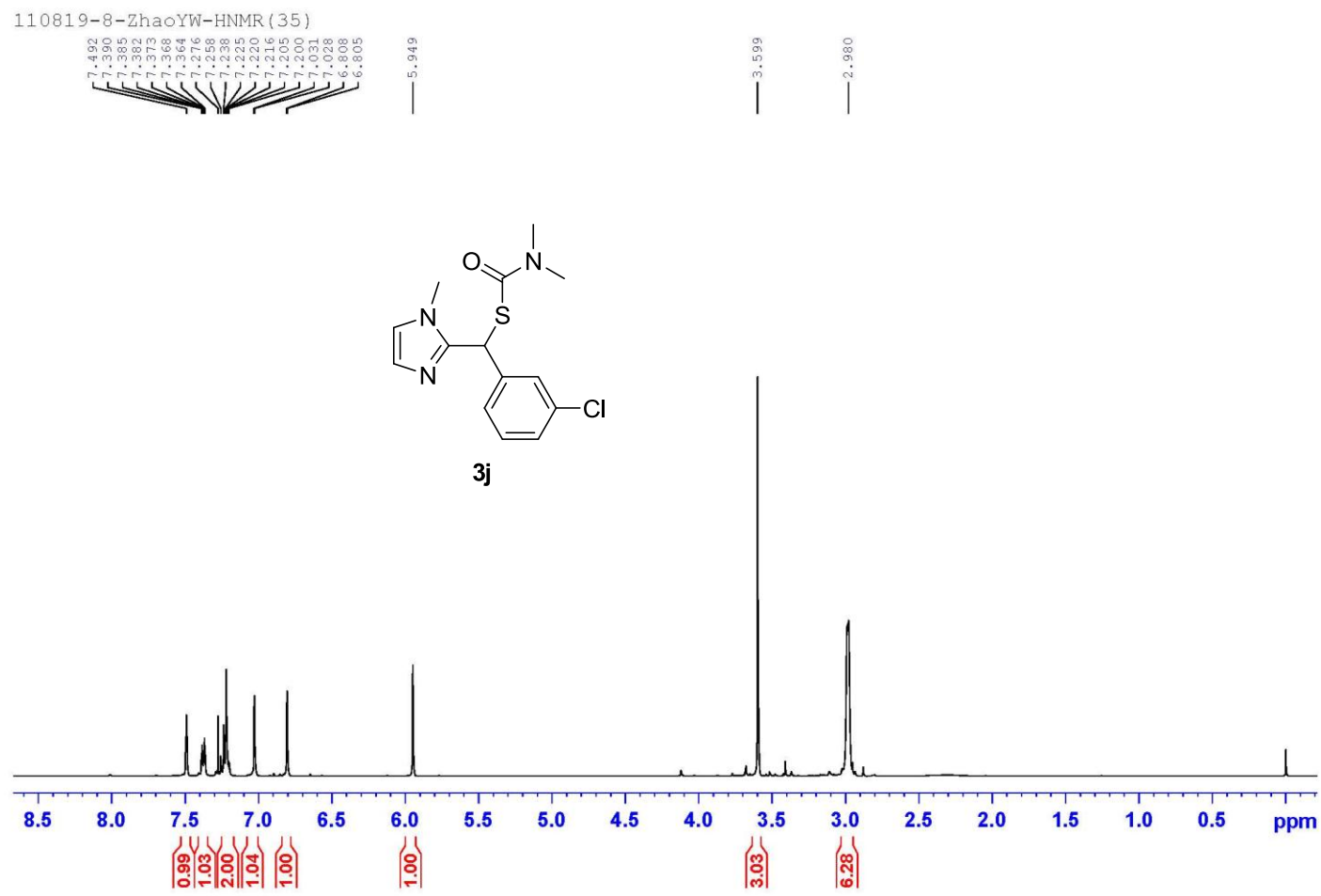


111028-1-ZYW-HNMR

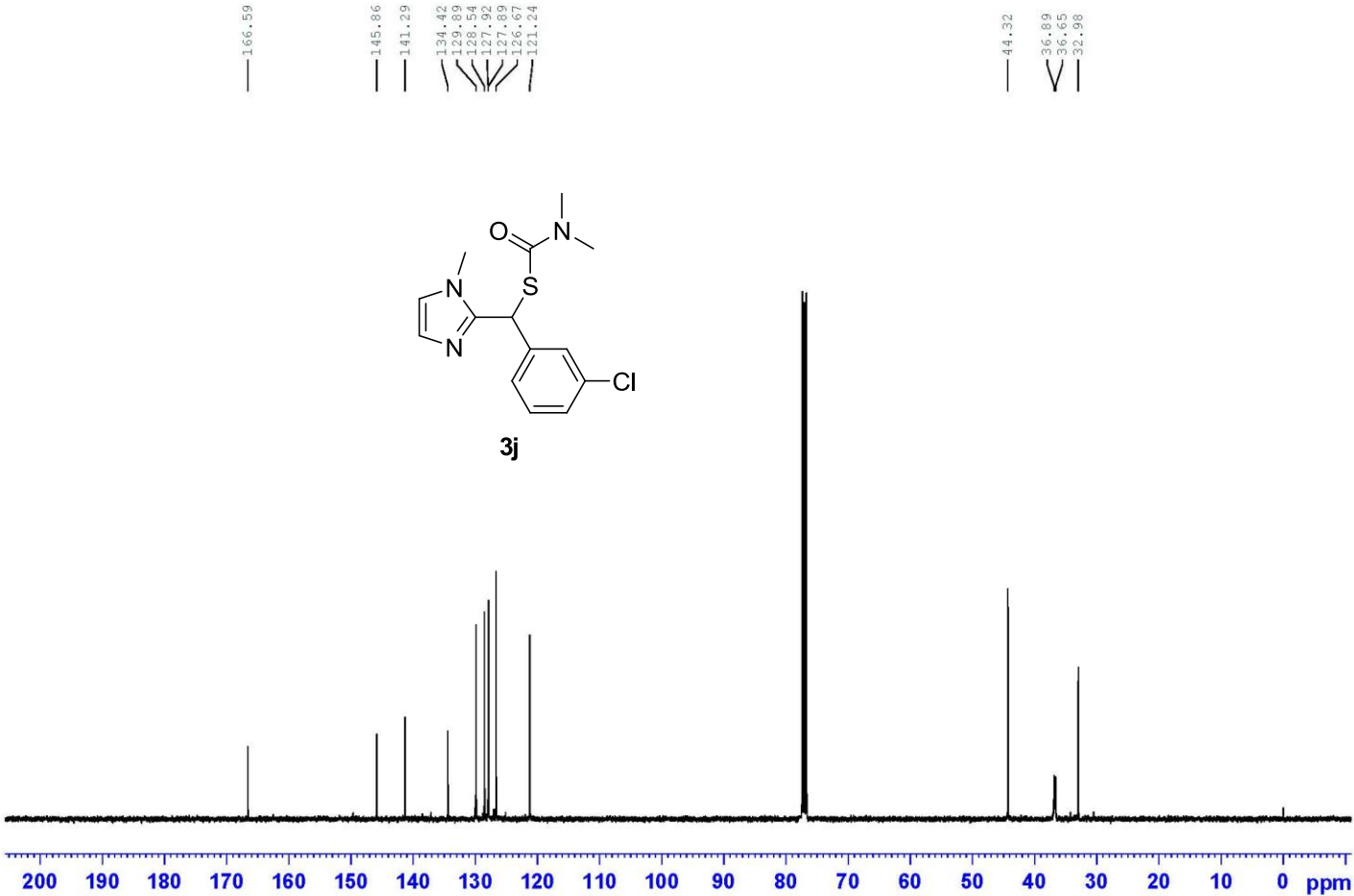


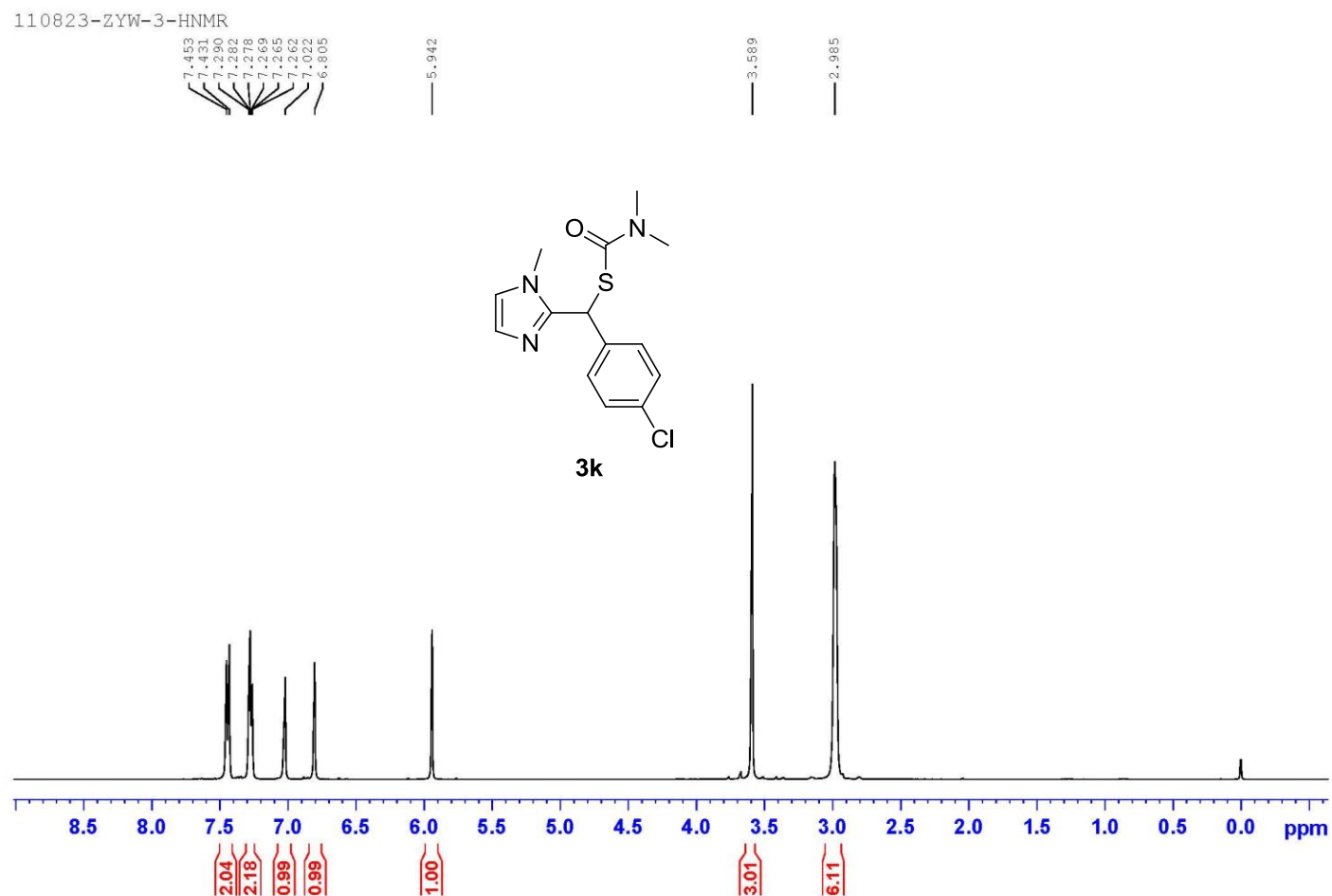
111028-1-ZYW-CNMR



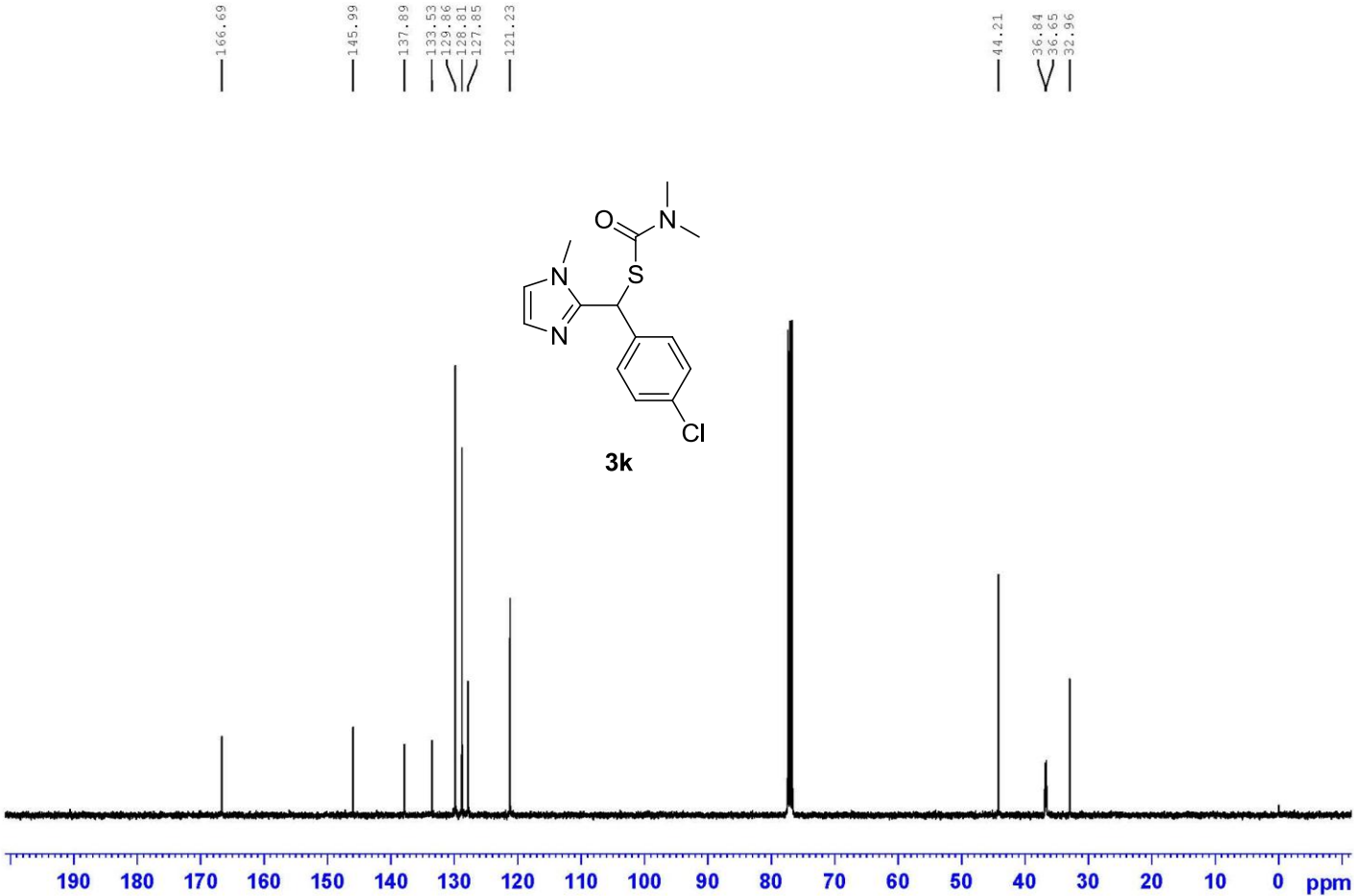


110819-8-ZhaoYW-CNMR (36)

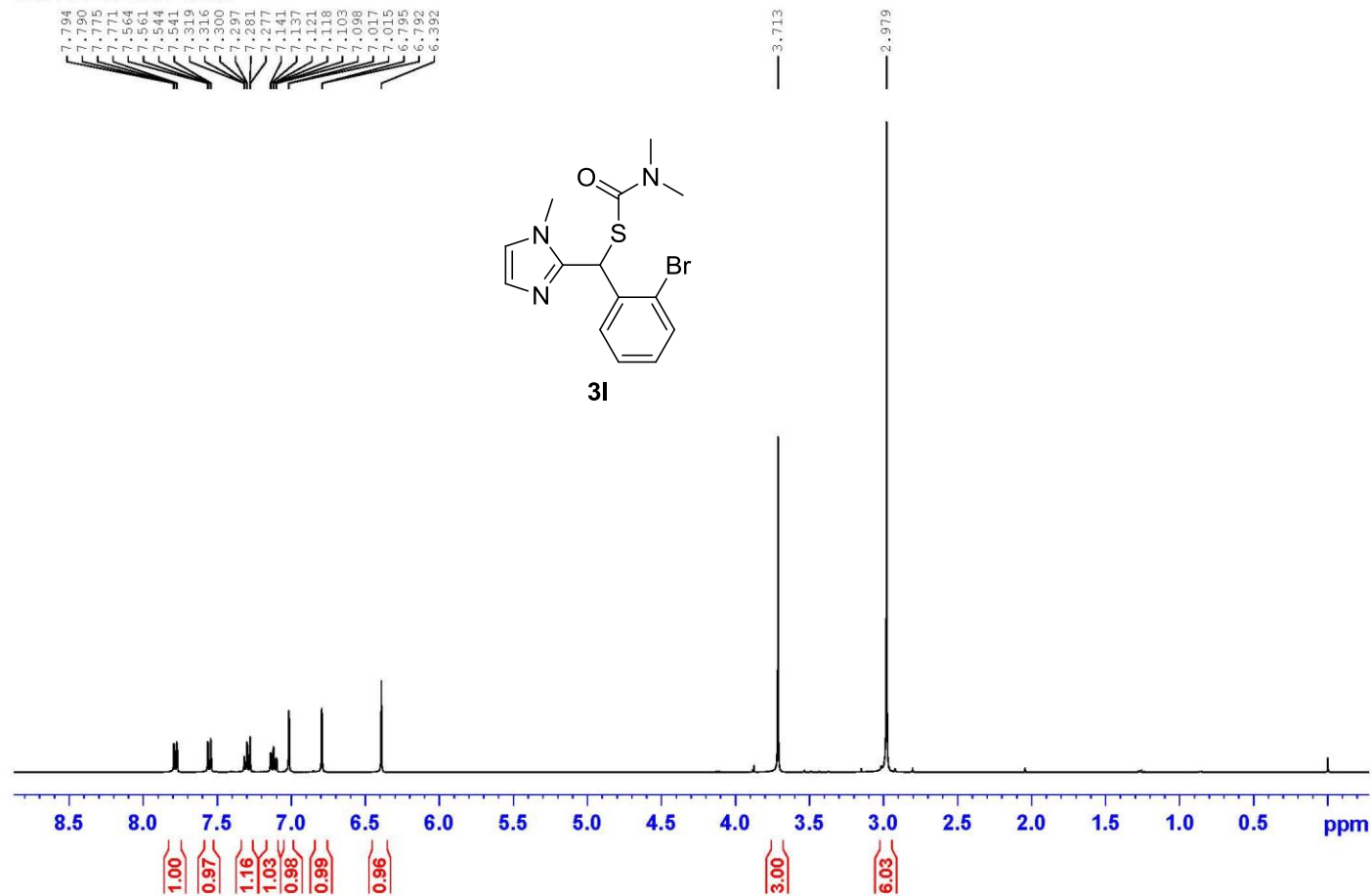




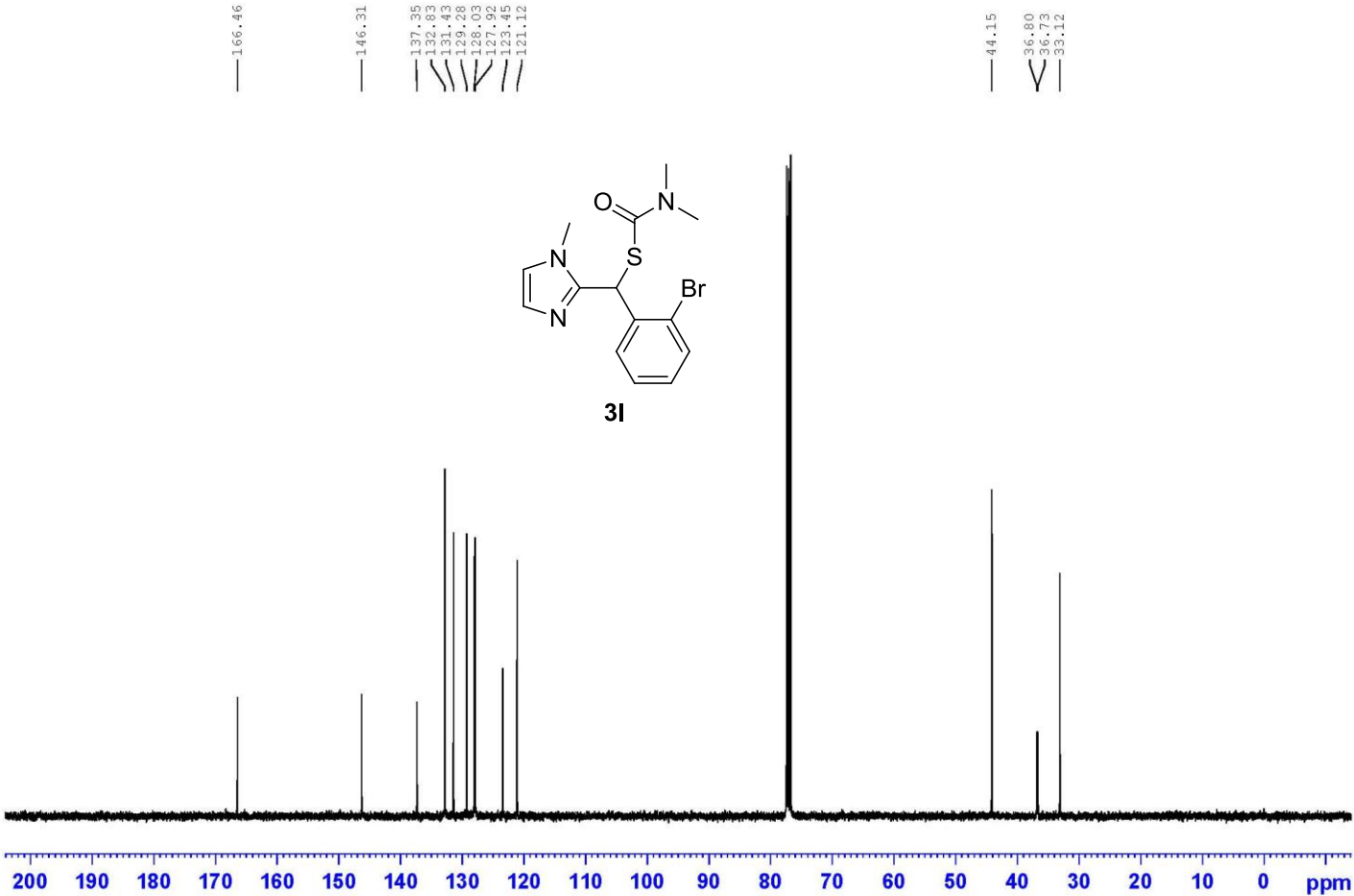
110823-ZYW-3-CNMR



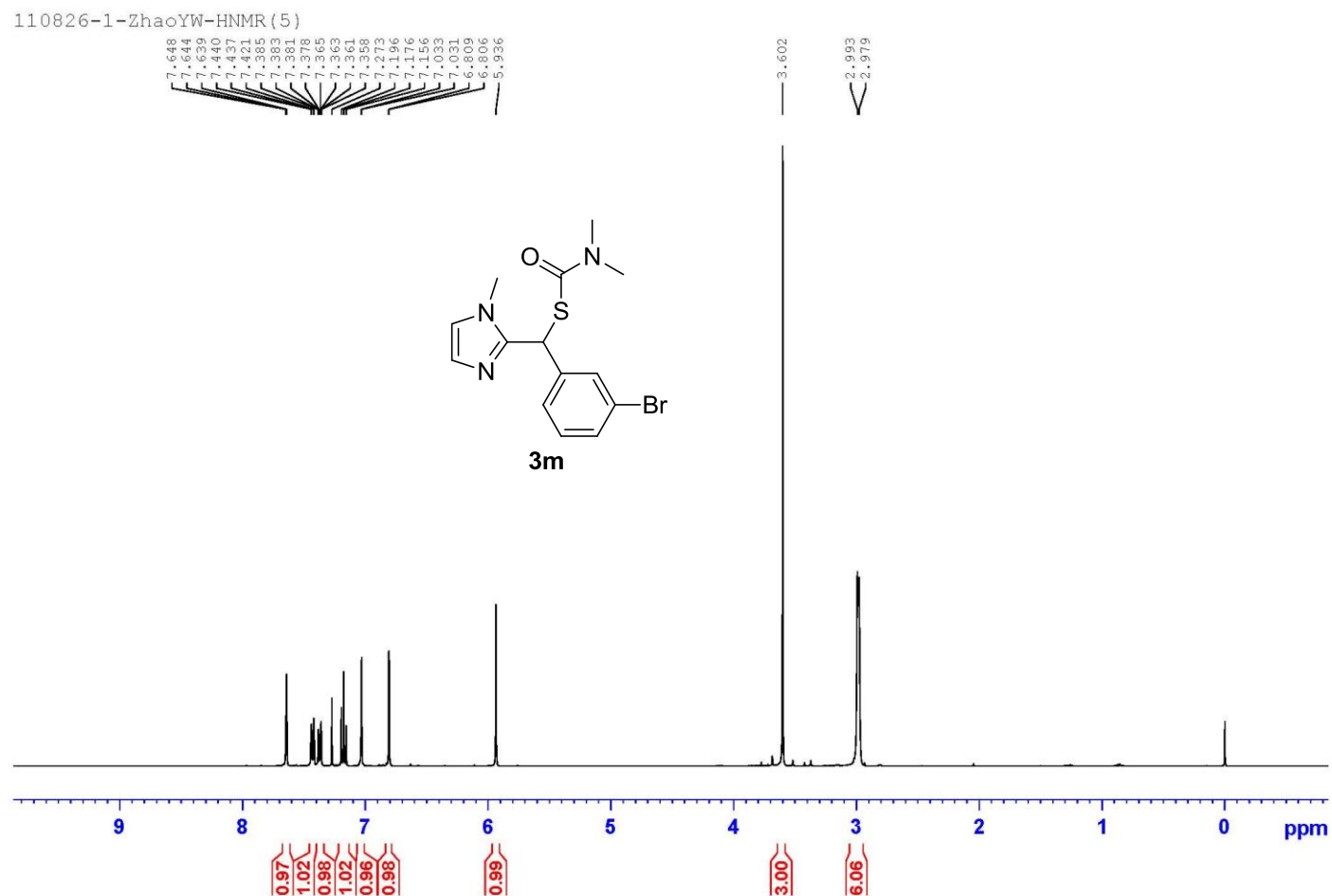
111028-2-ZYW-HNMR



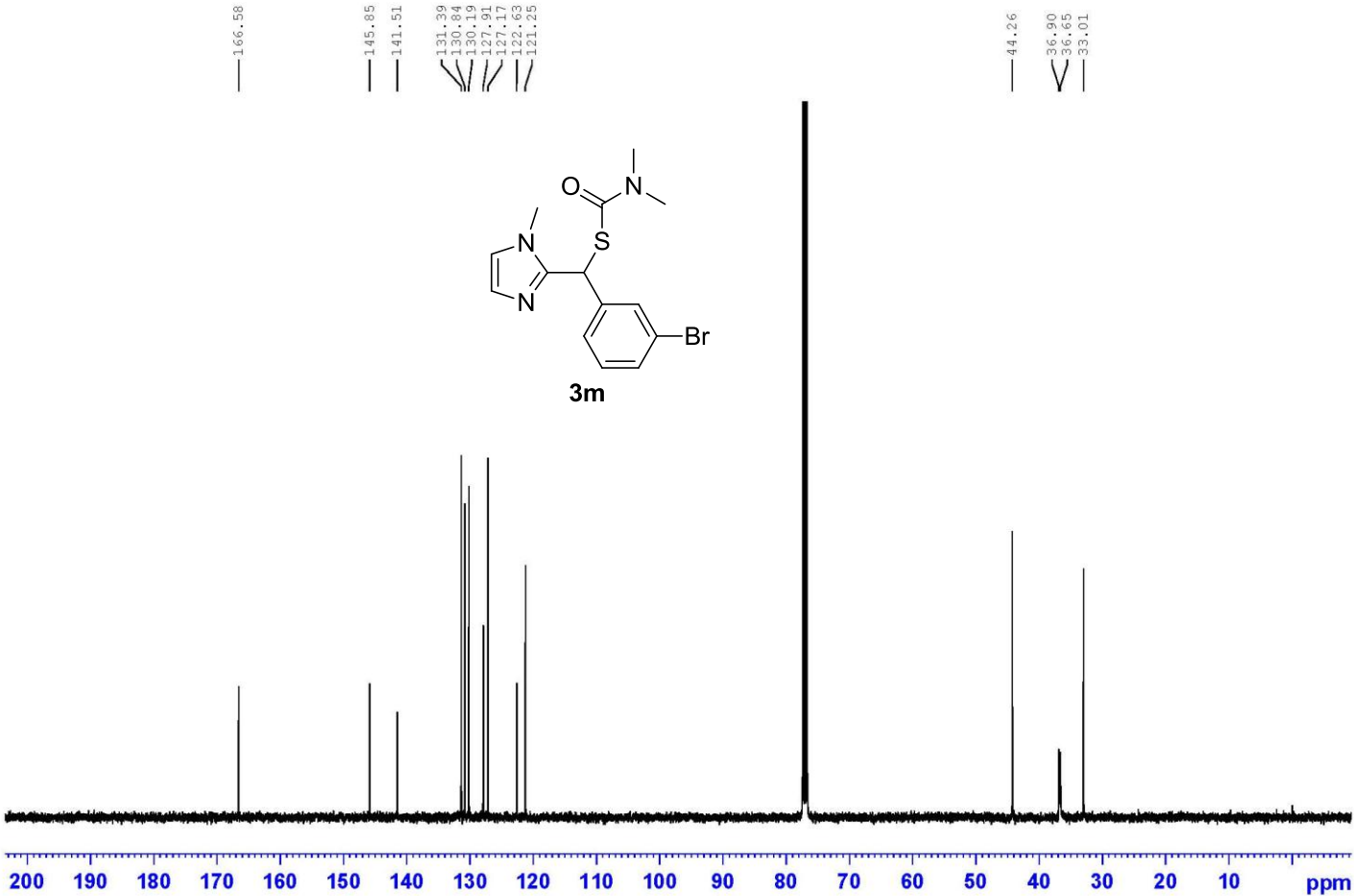
111028-2-ZYW-CNMR



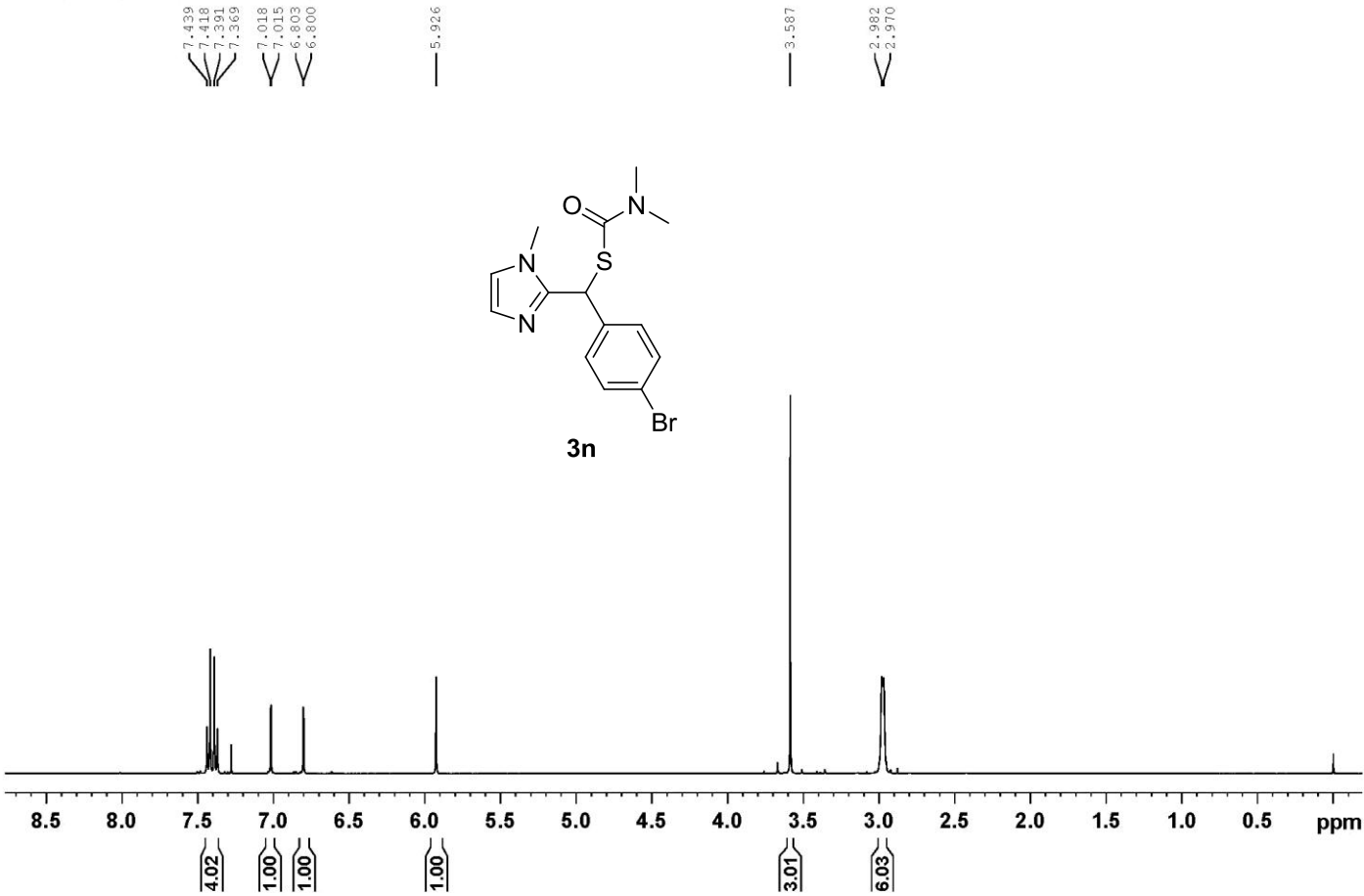




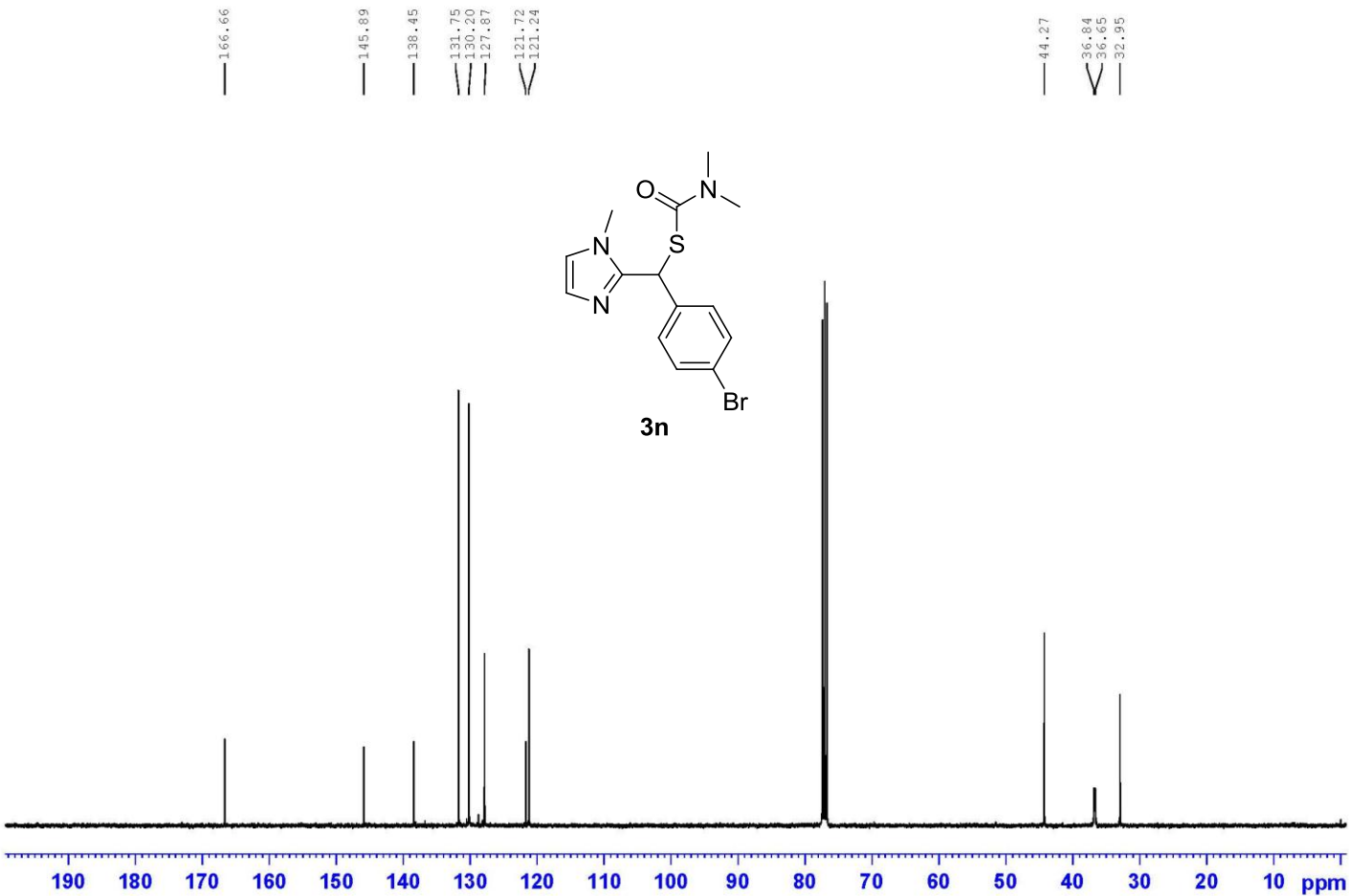
110826-1-ZhaoYW-CNMR (6)



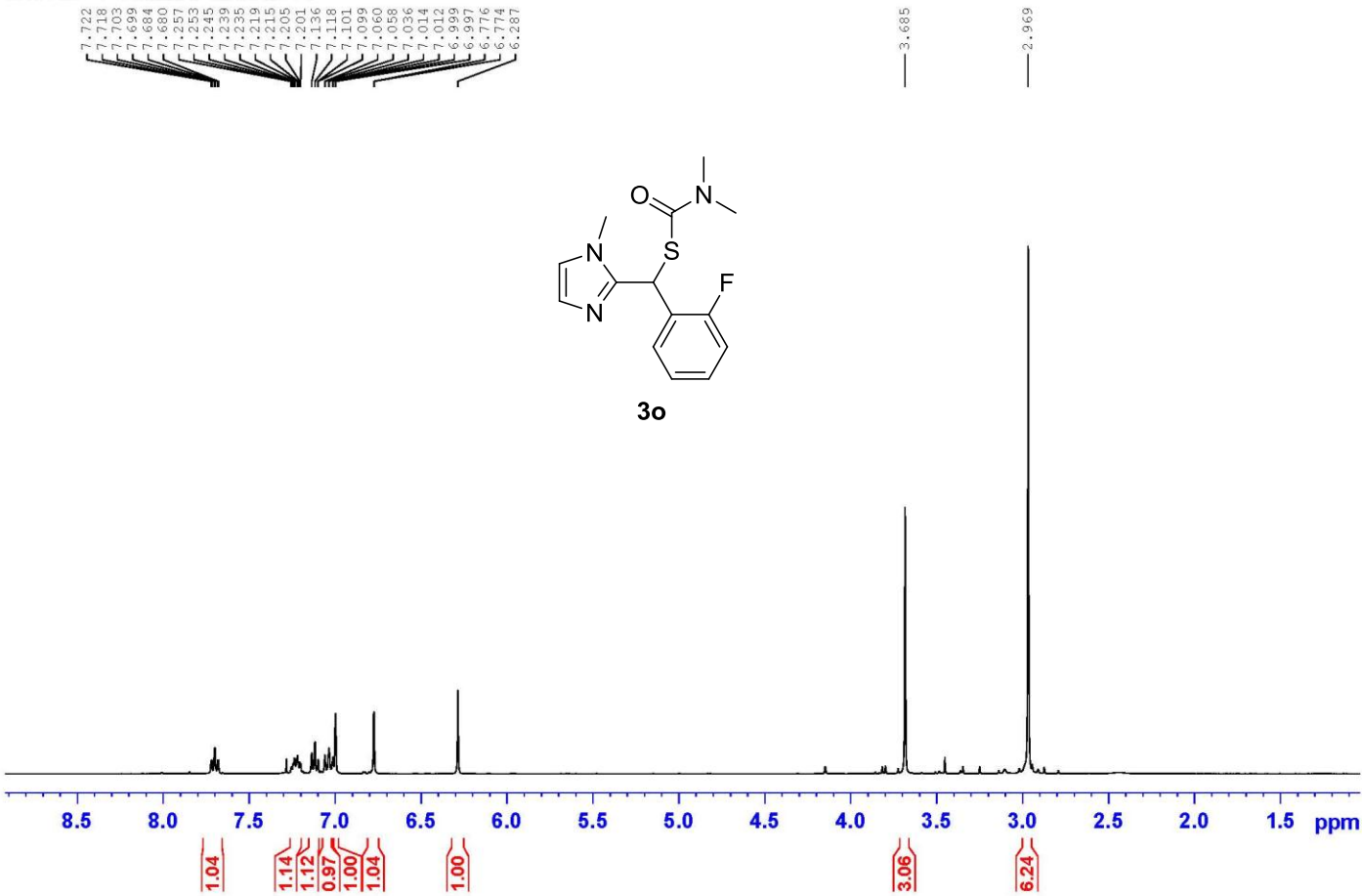
110819-2-ZhaoYW-HNMR (23)



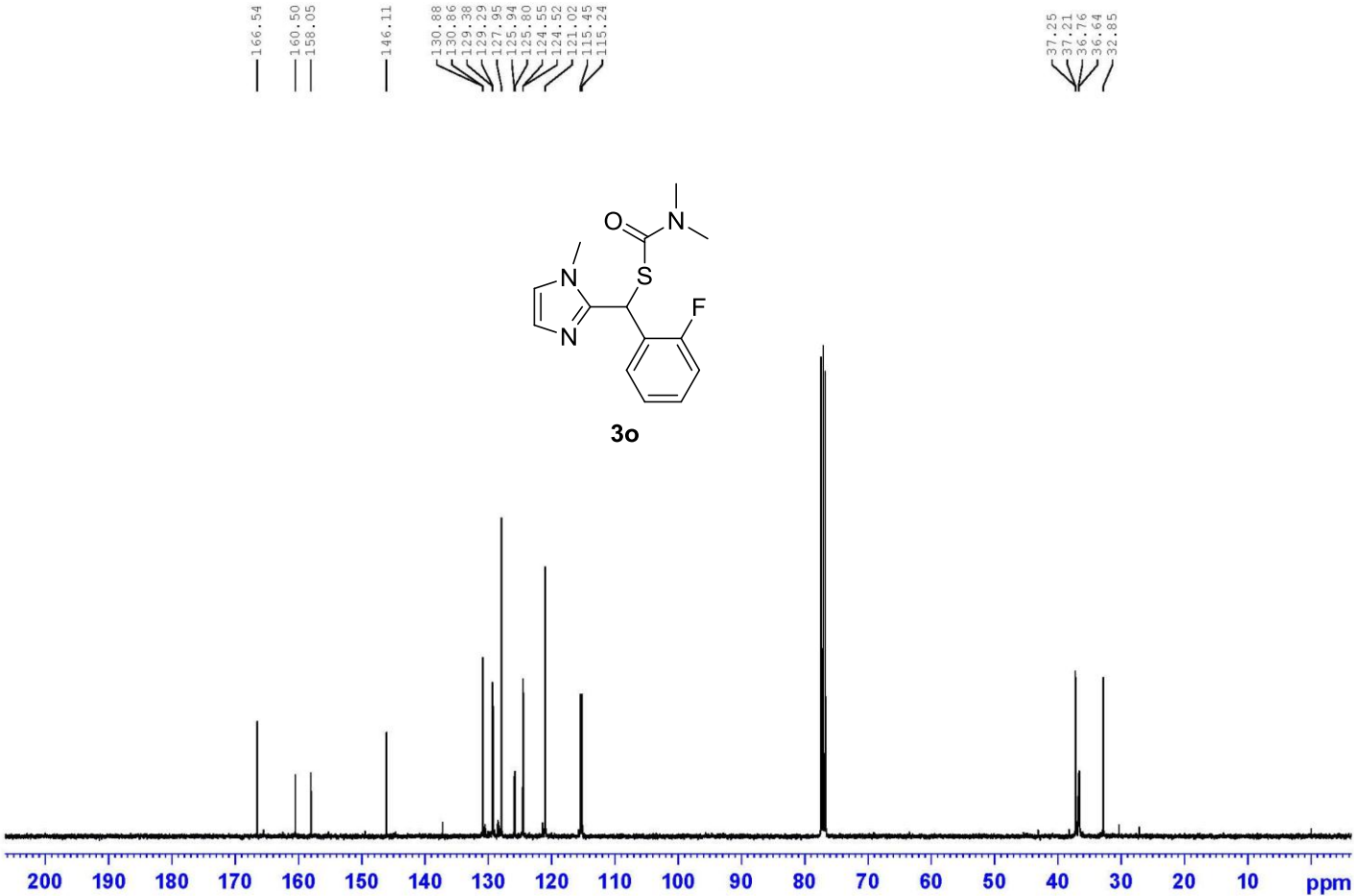
110819-2-ZhaoYW-CNMR (24)



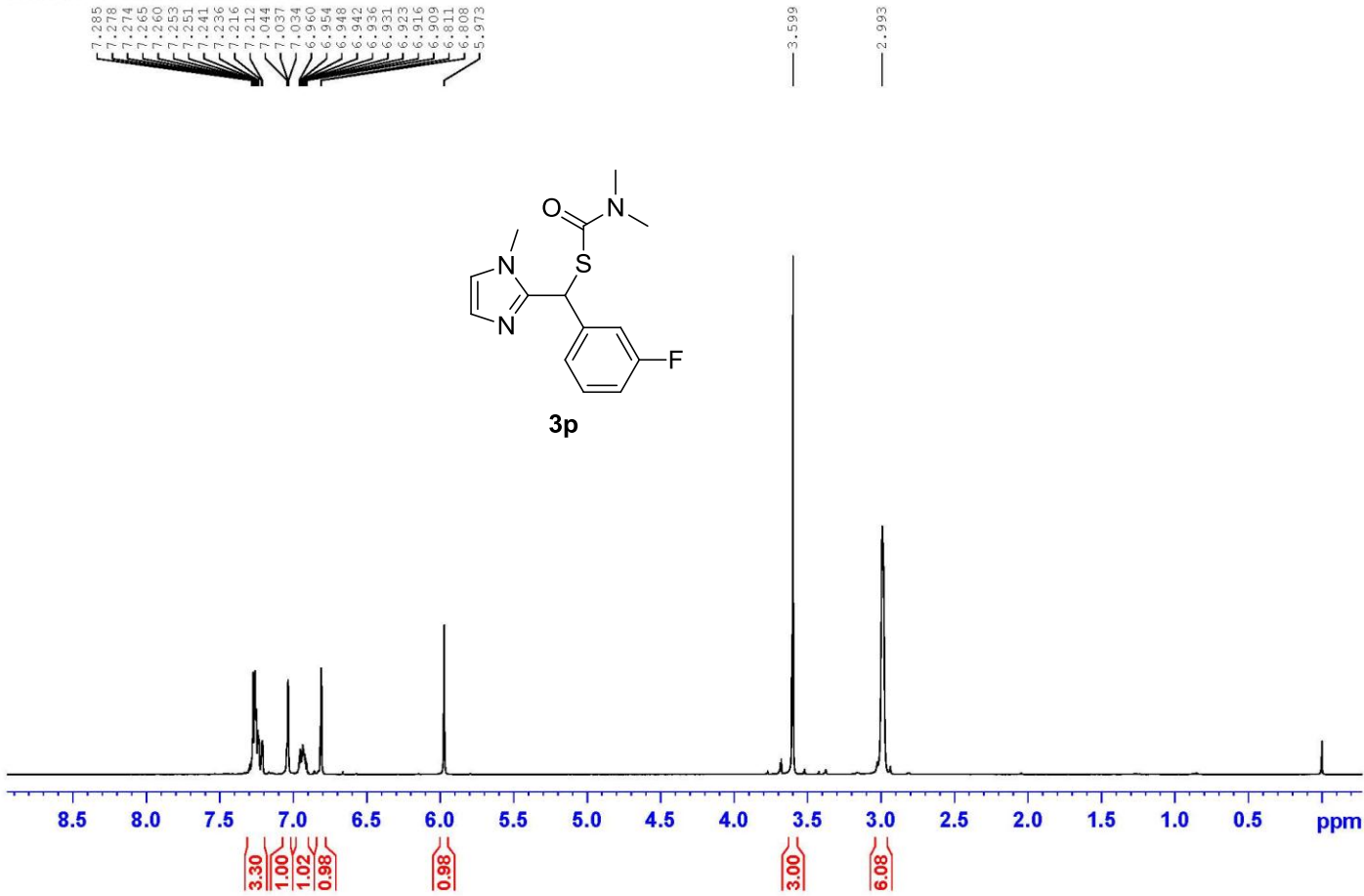
110819-5-ZhaoYW-HNMR (29)



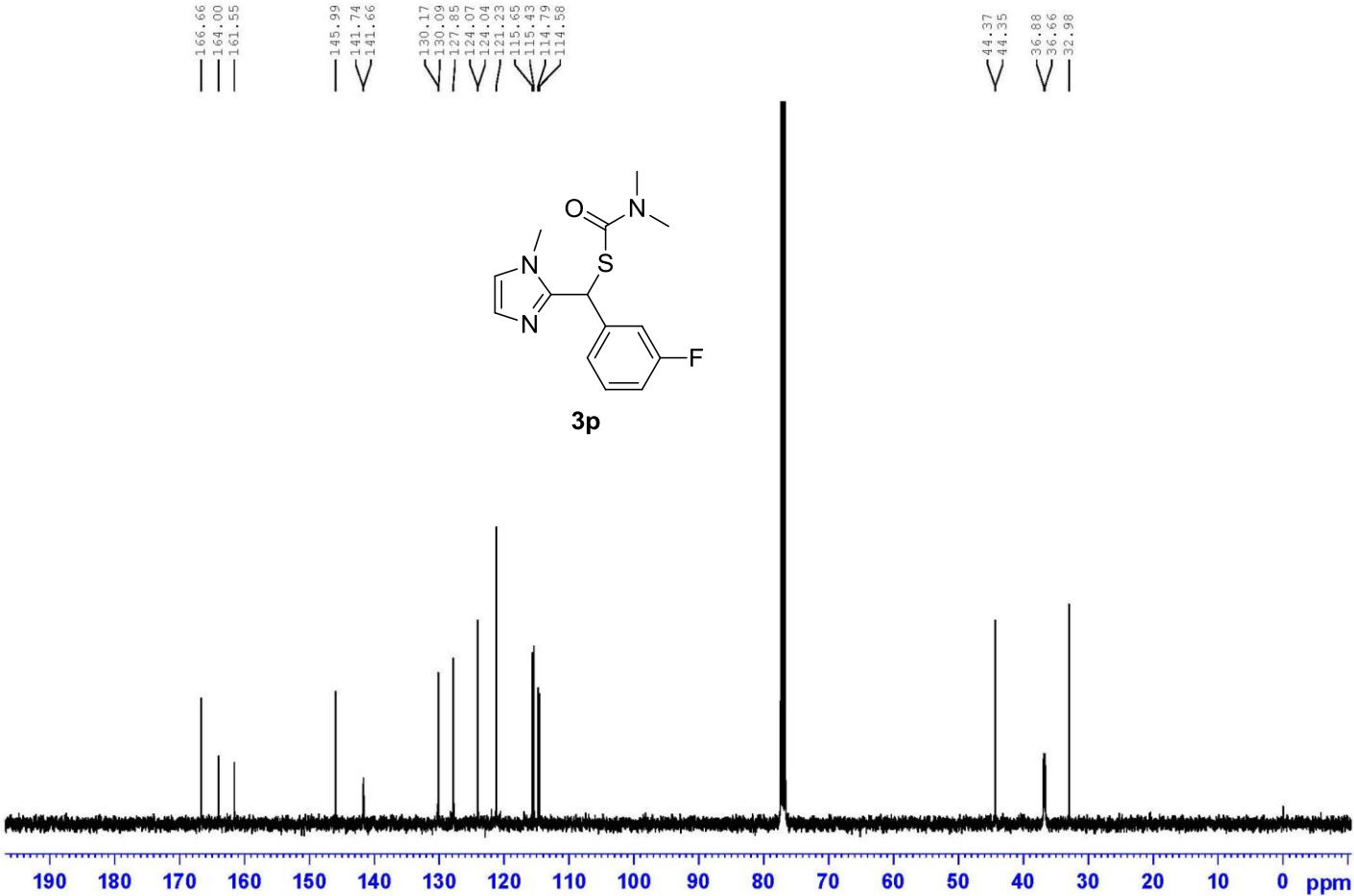
110819-5-ZhaoYW-CNMR (30)



110826-3-ZhaoYW-HNMR (9)

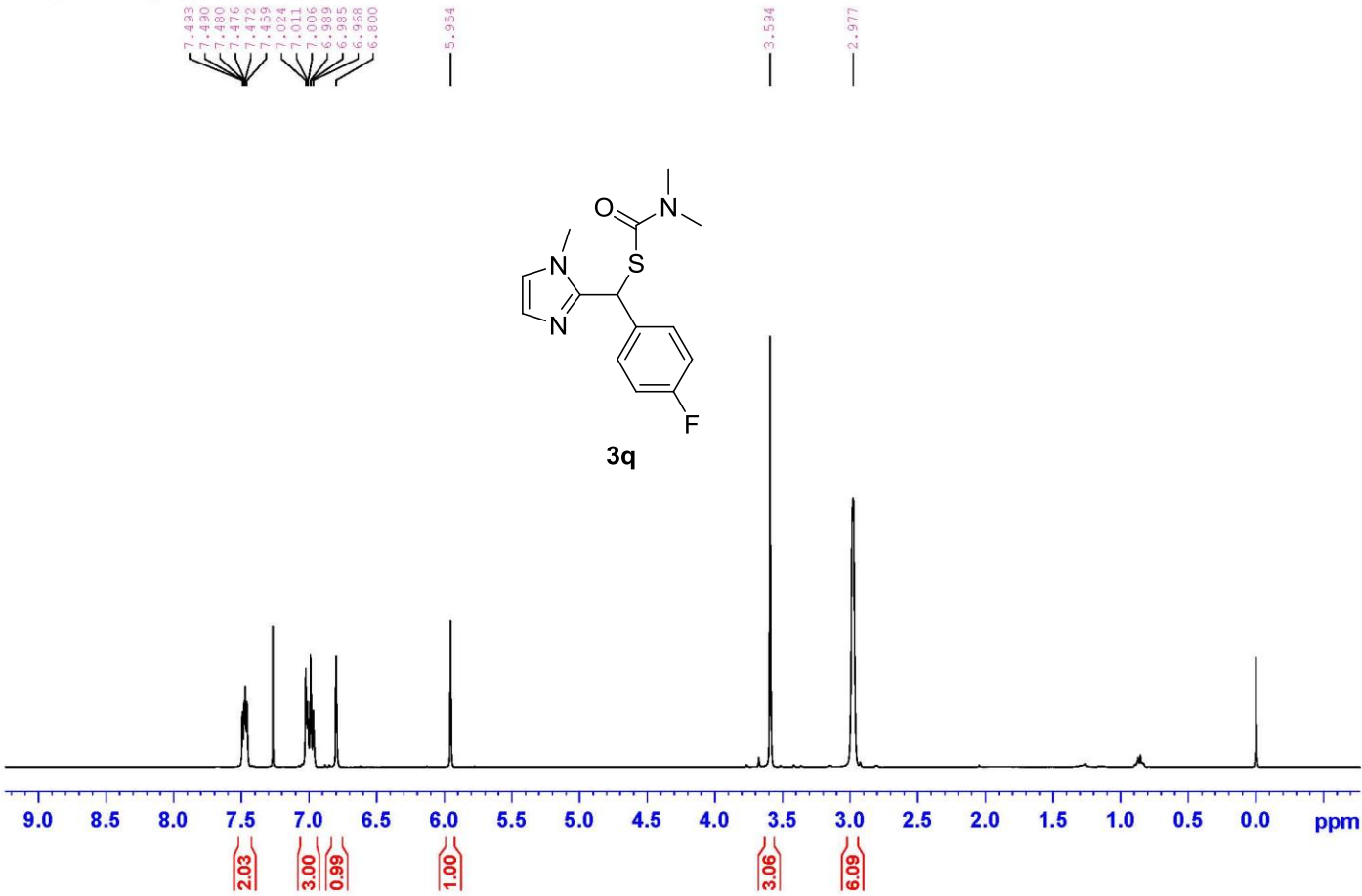


110826-3-ZhaoYW-CNMR(10)

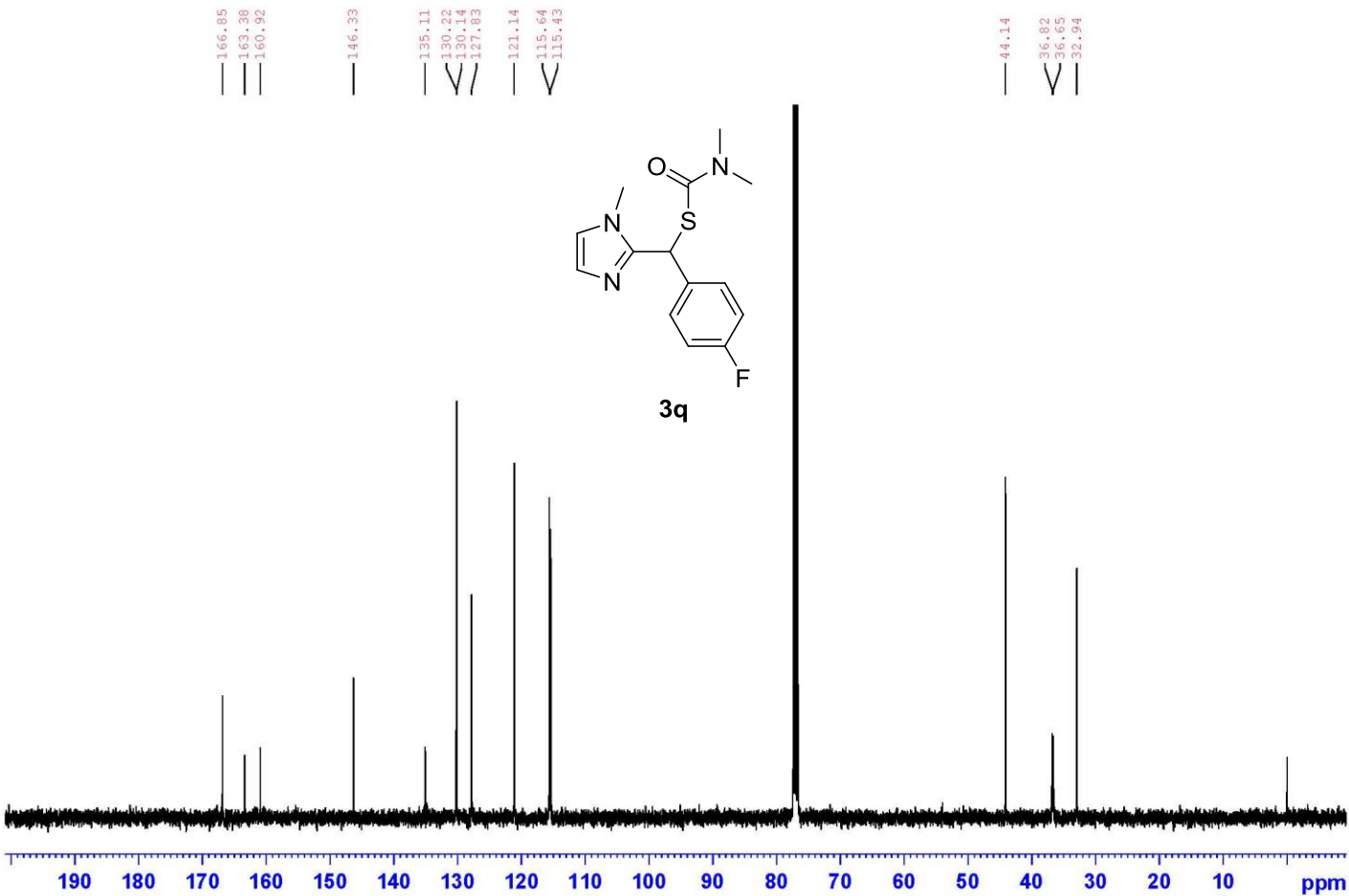


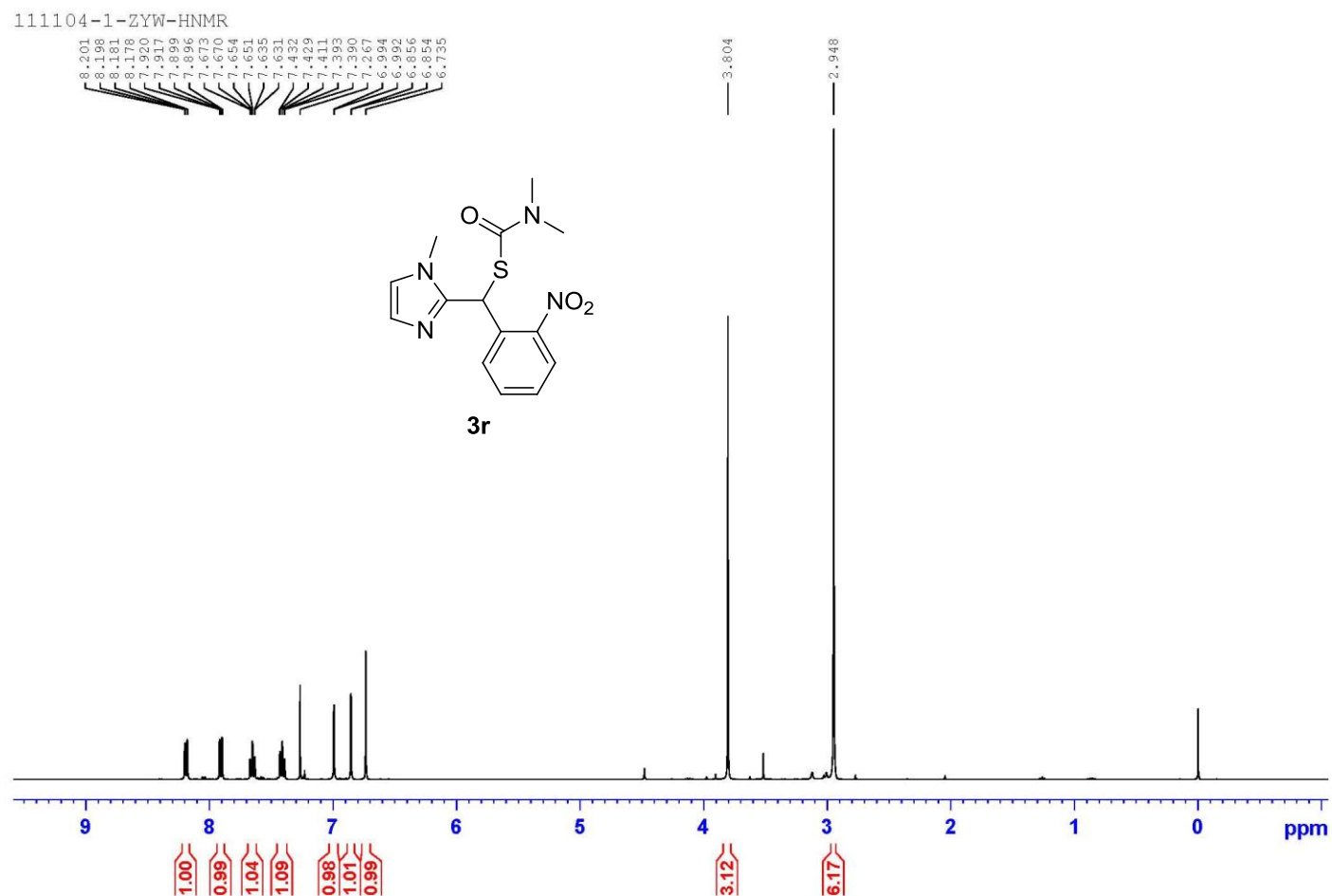


110816-zhaoyingwei-4-HNMR

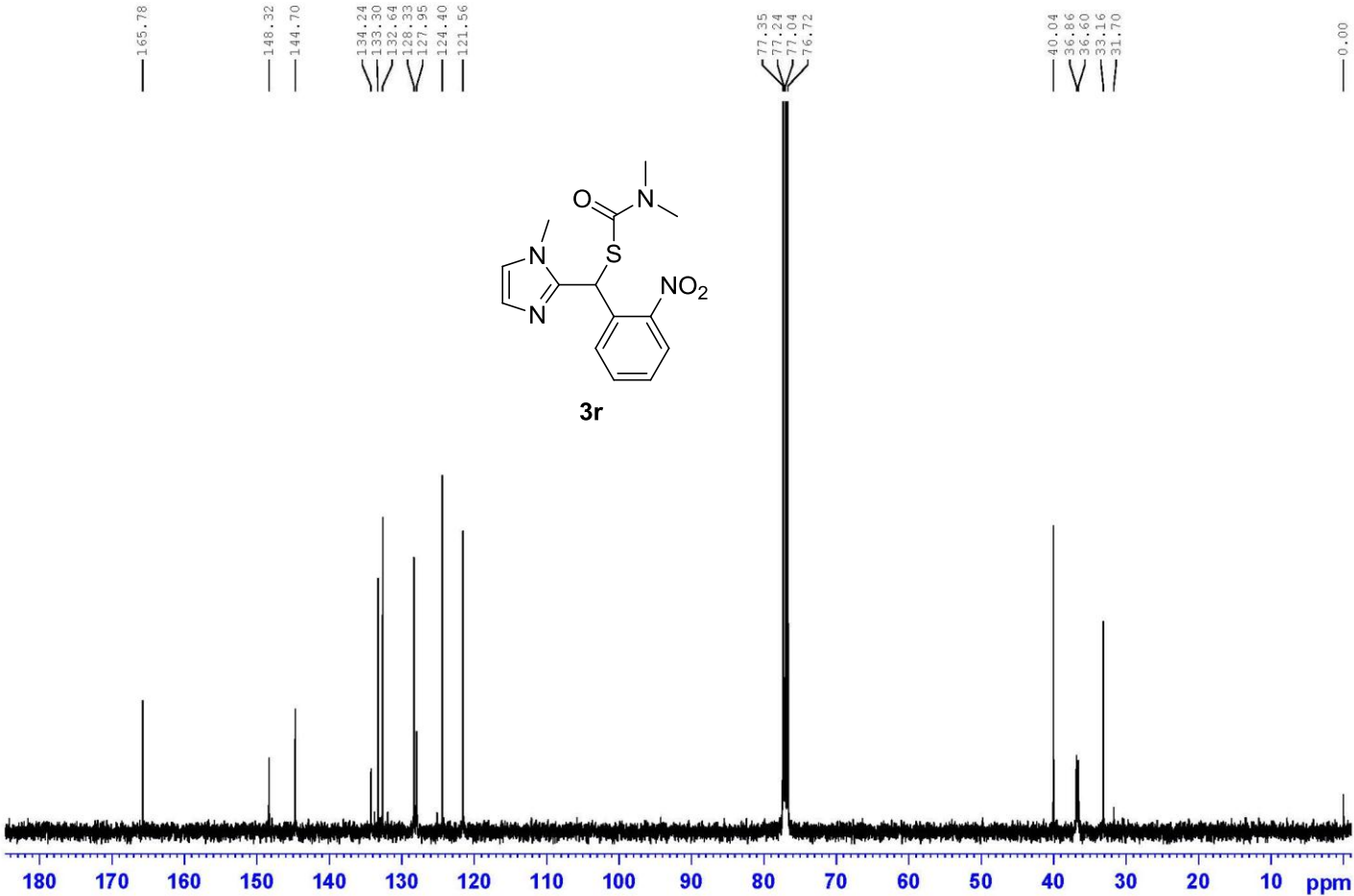


110816-zhaoyingwei-4-CNMR

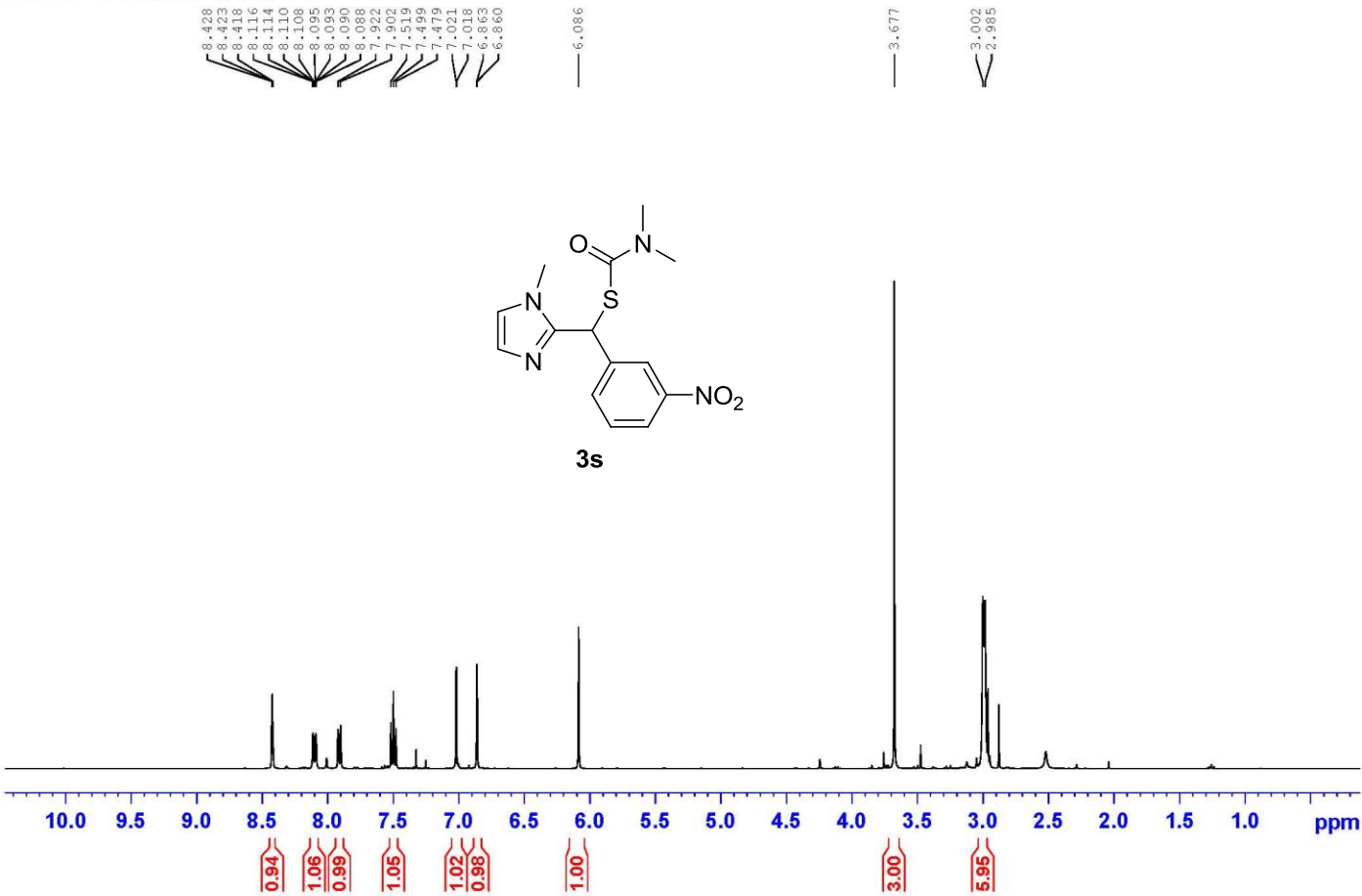




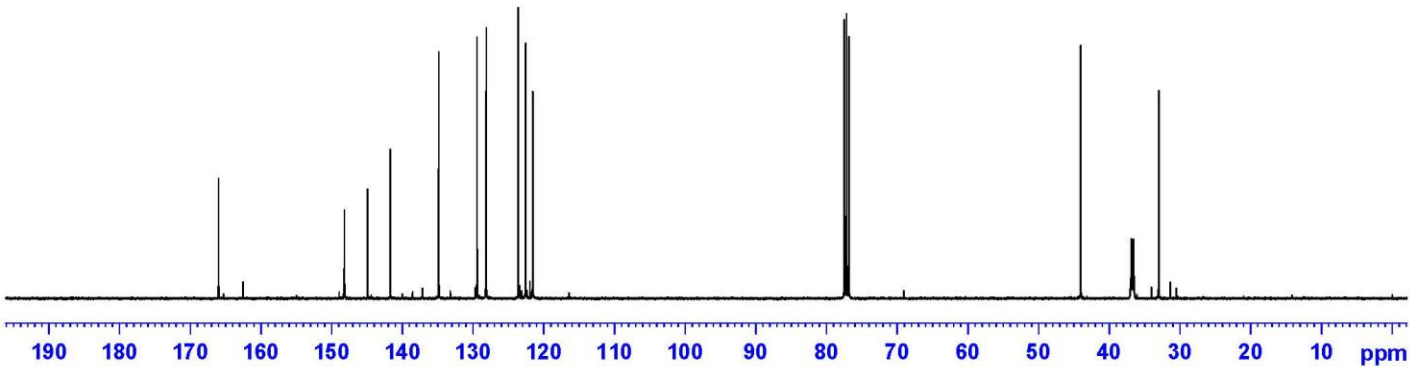
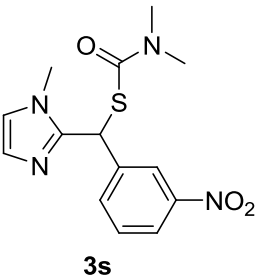
111104-1-ZYW-CNMR



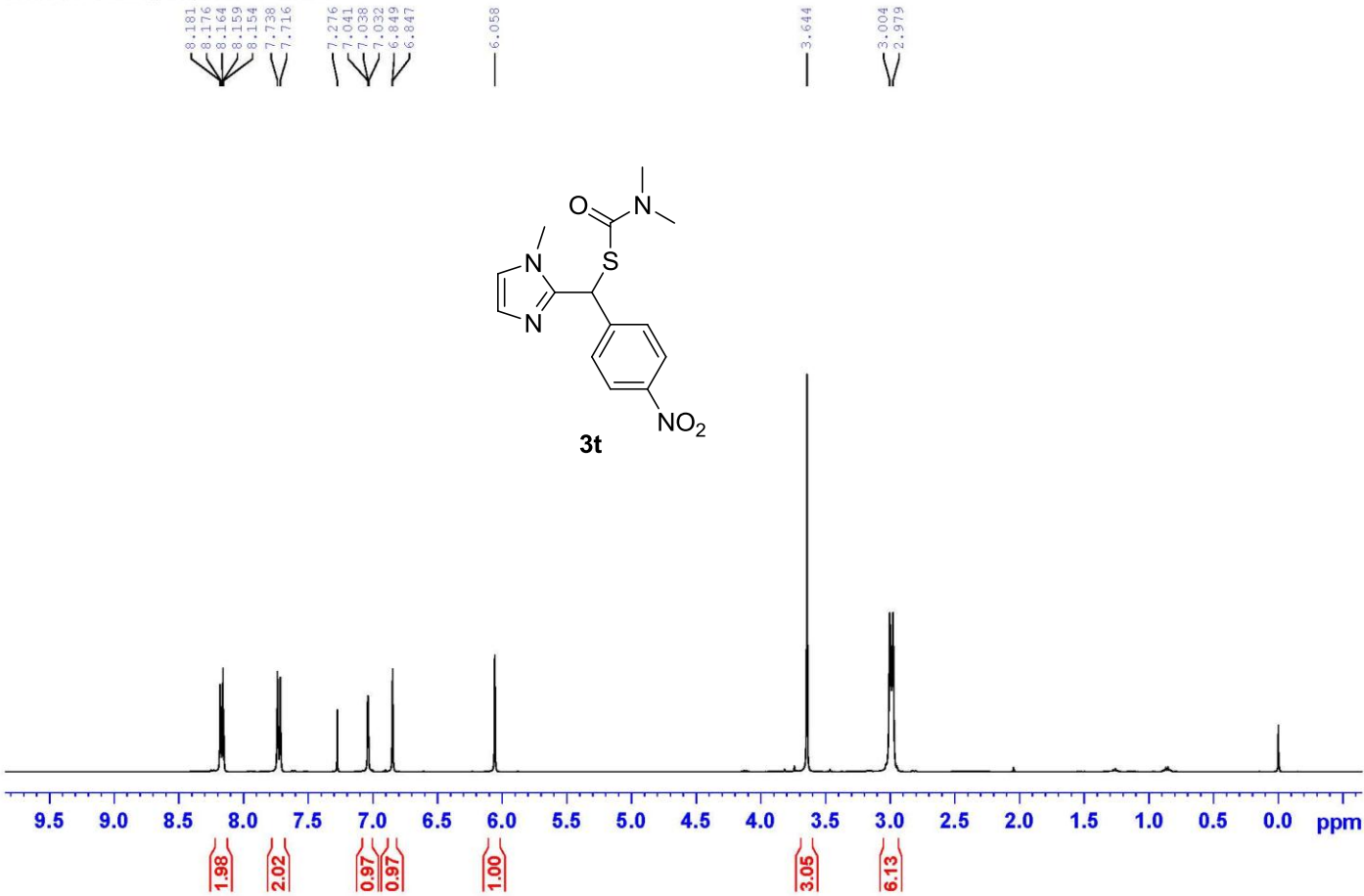
110819-4-ZhaoYW-HNMR (27)



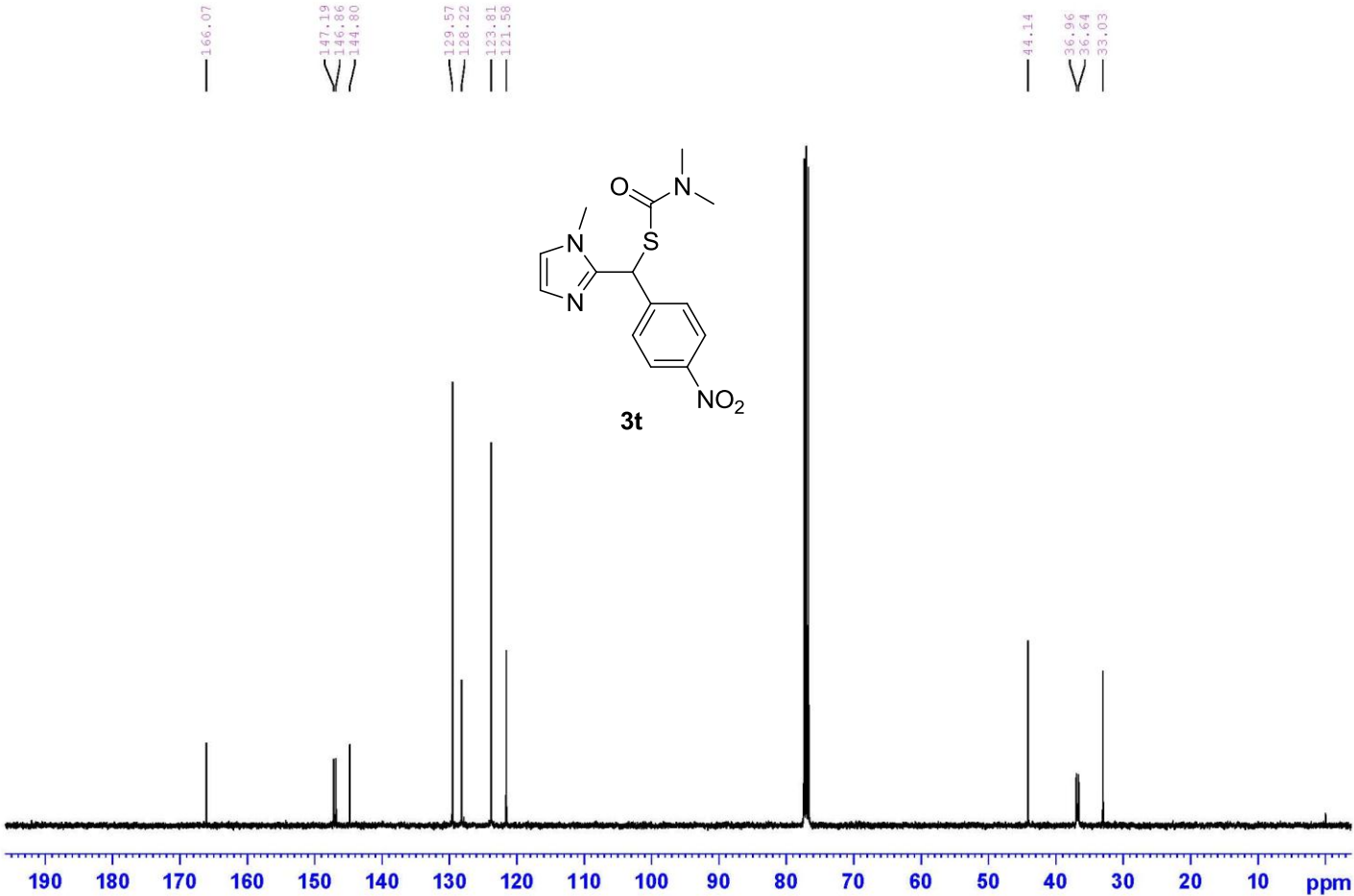
110819-4-ZhaoYW-CNMR (28)



110816-zhaoyingwei-5-HNMR

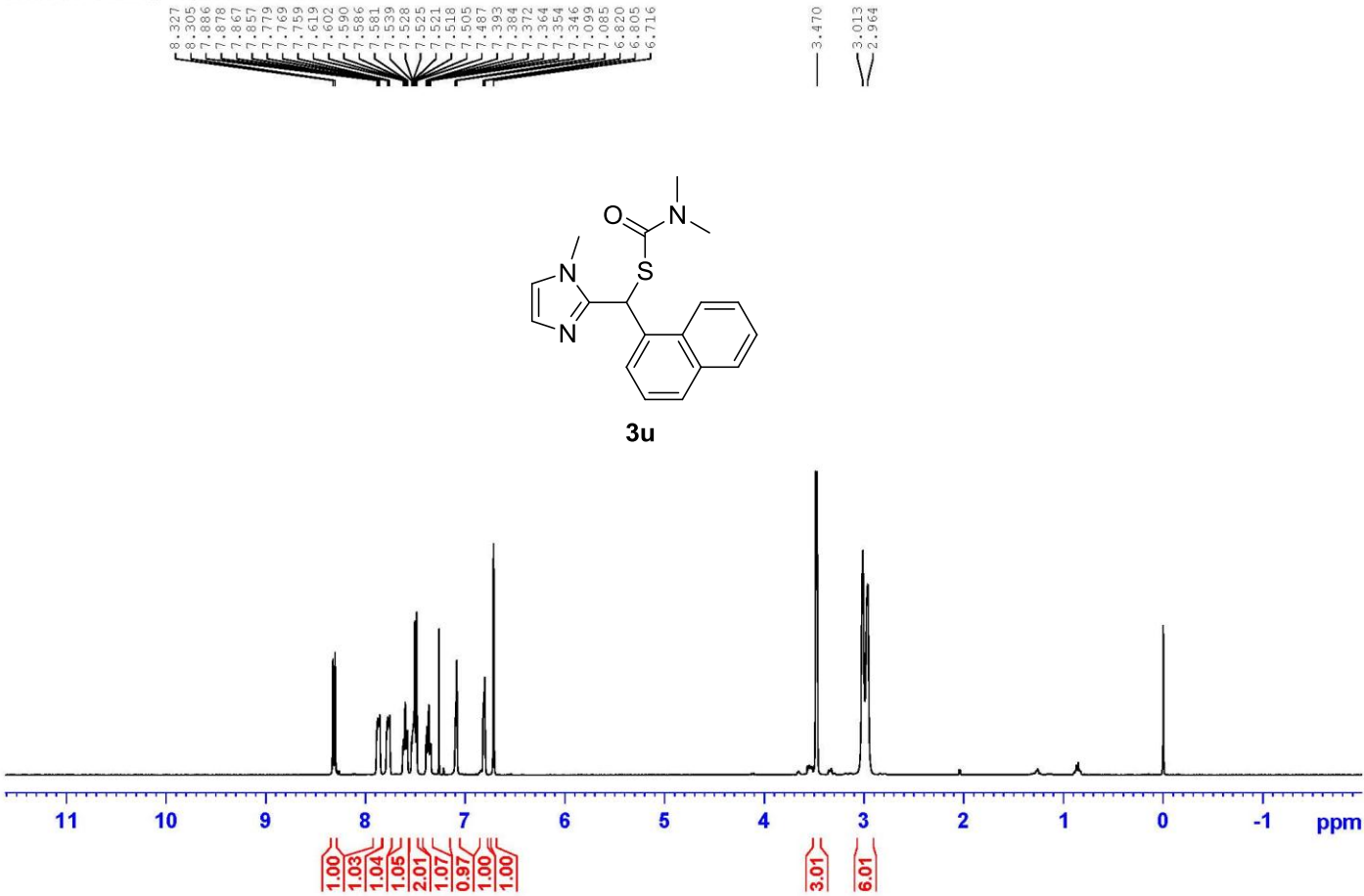


110816-zhaoyingwei-5-CNMR

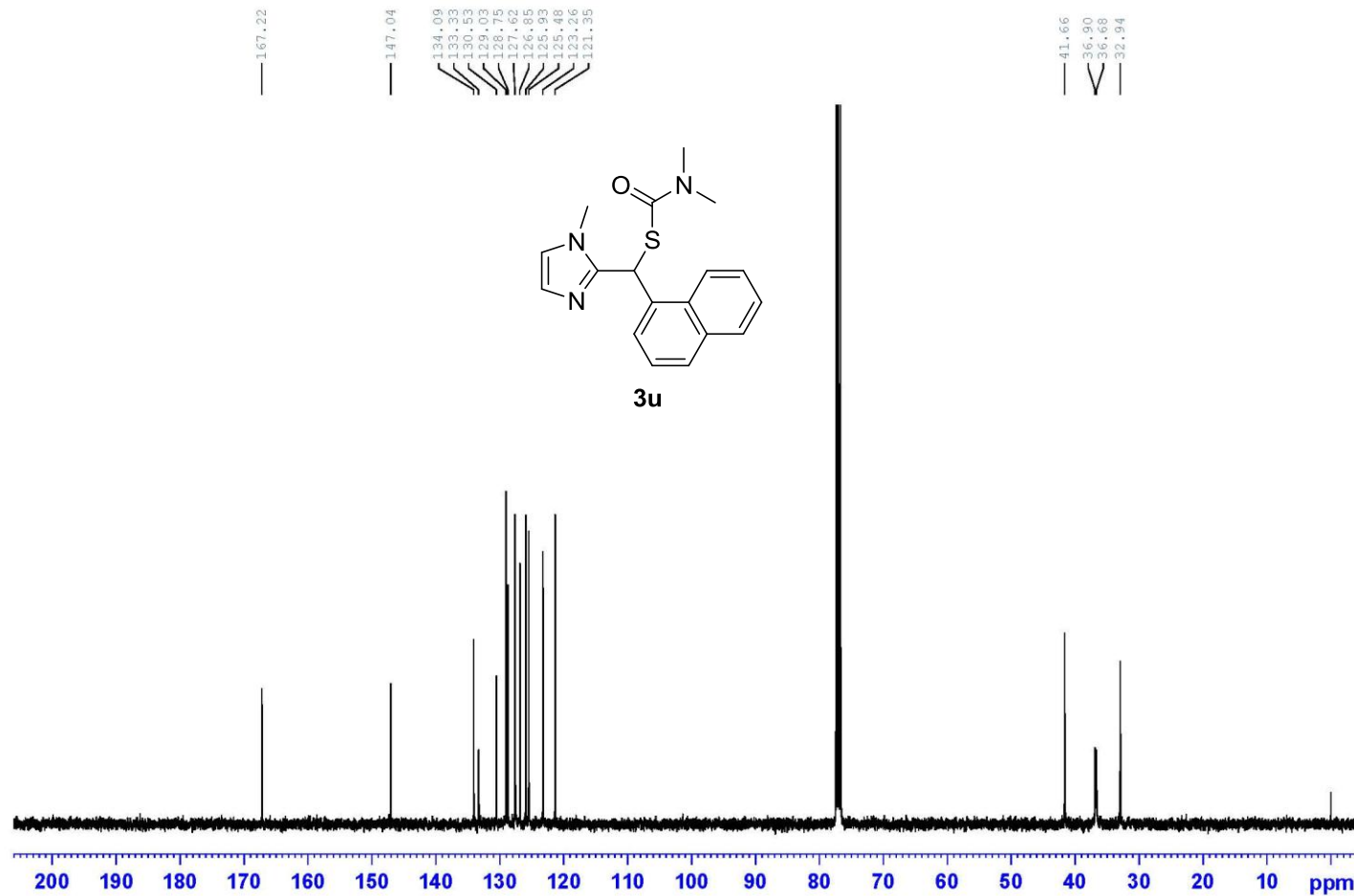




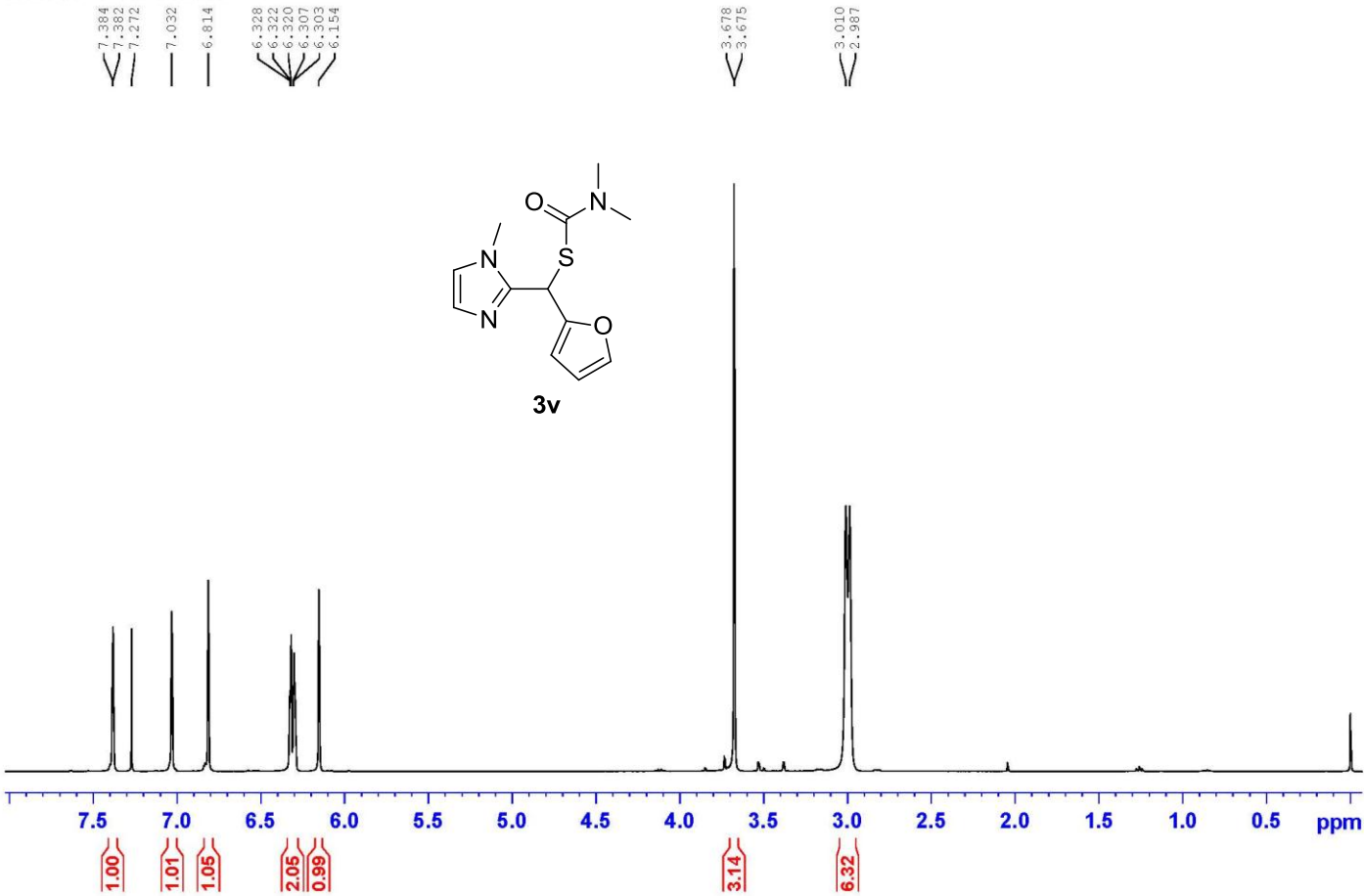
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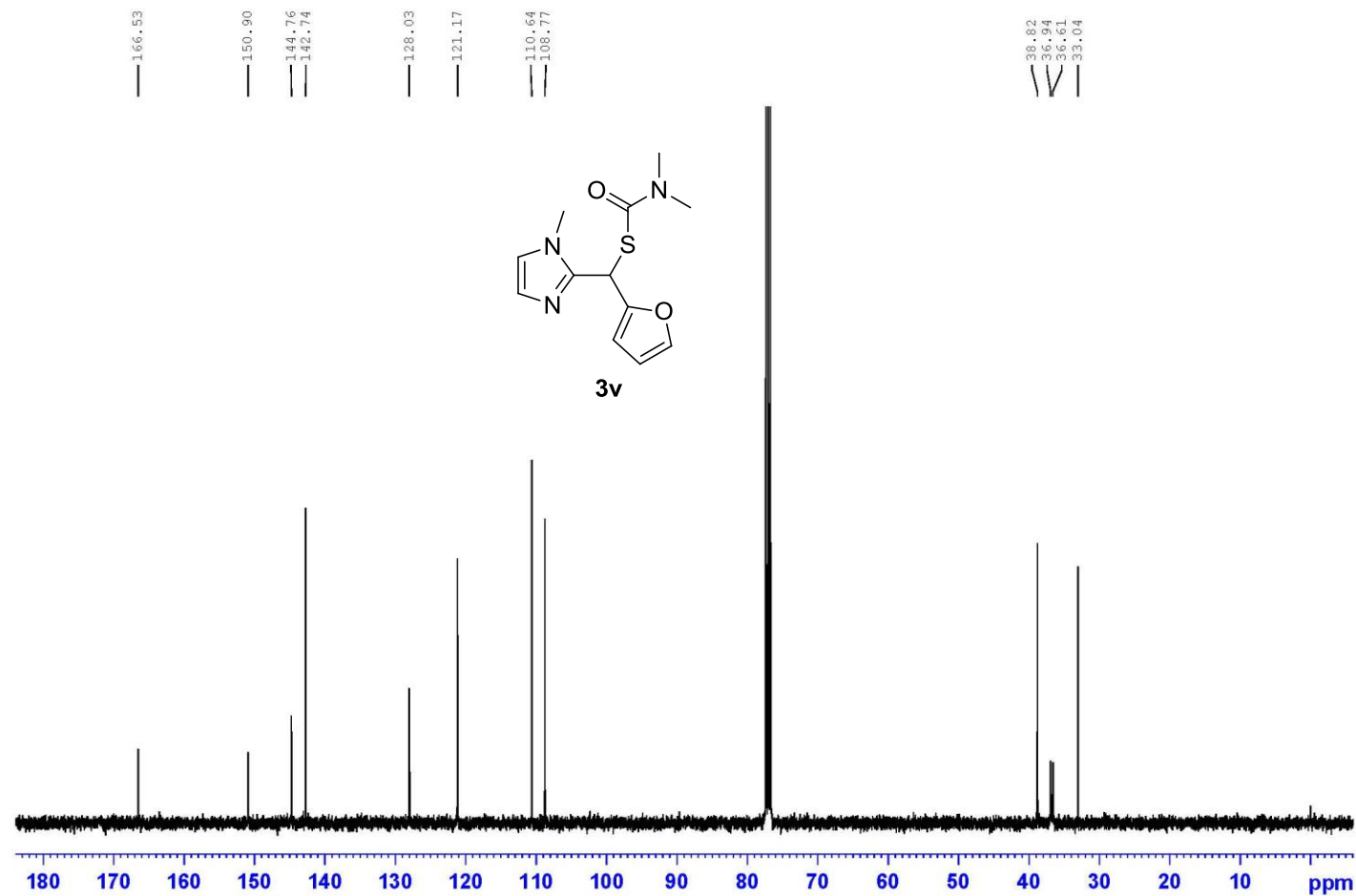
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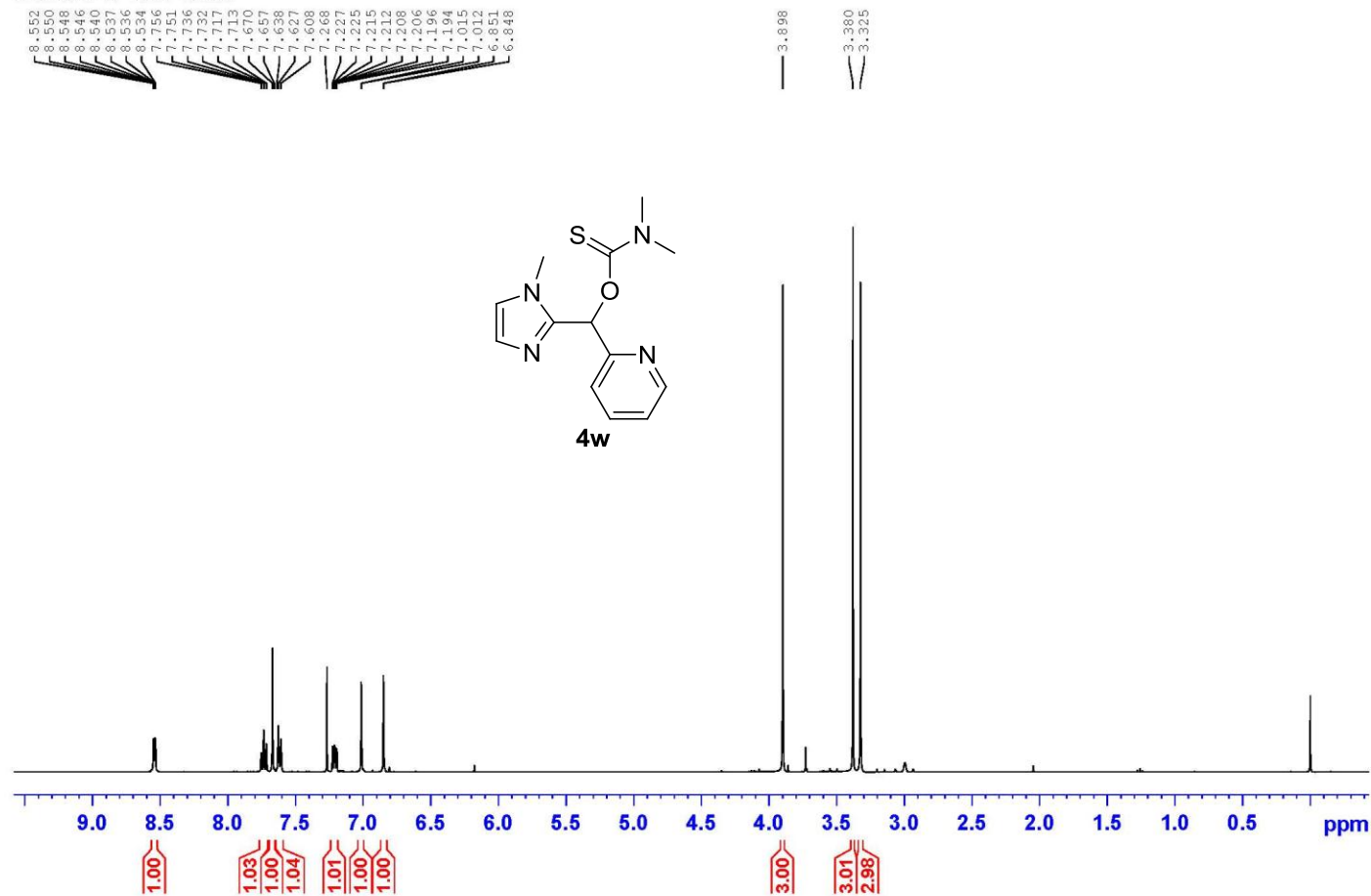
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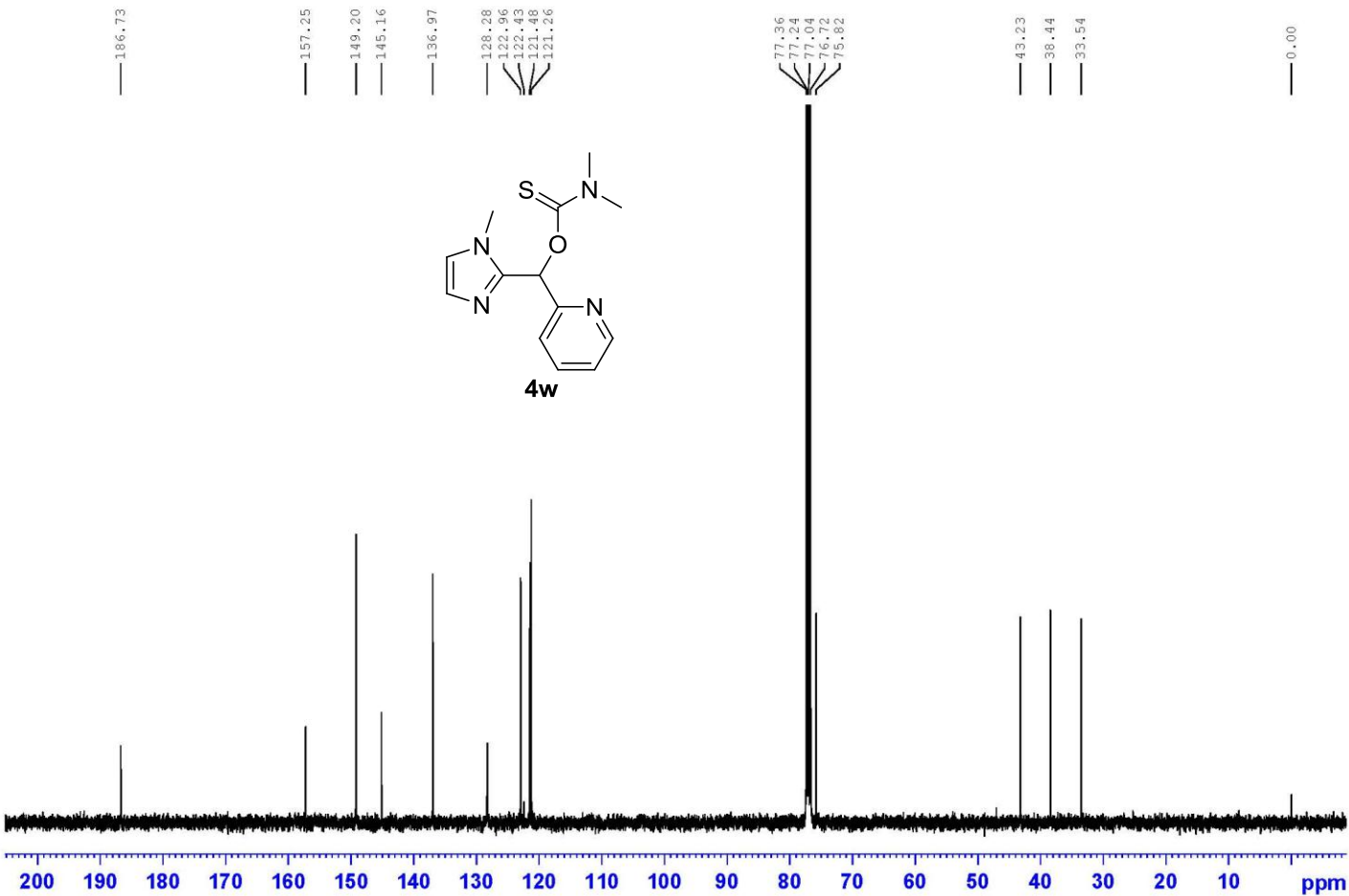
111028-3-ZYW-CNMR

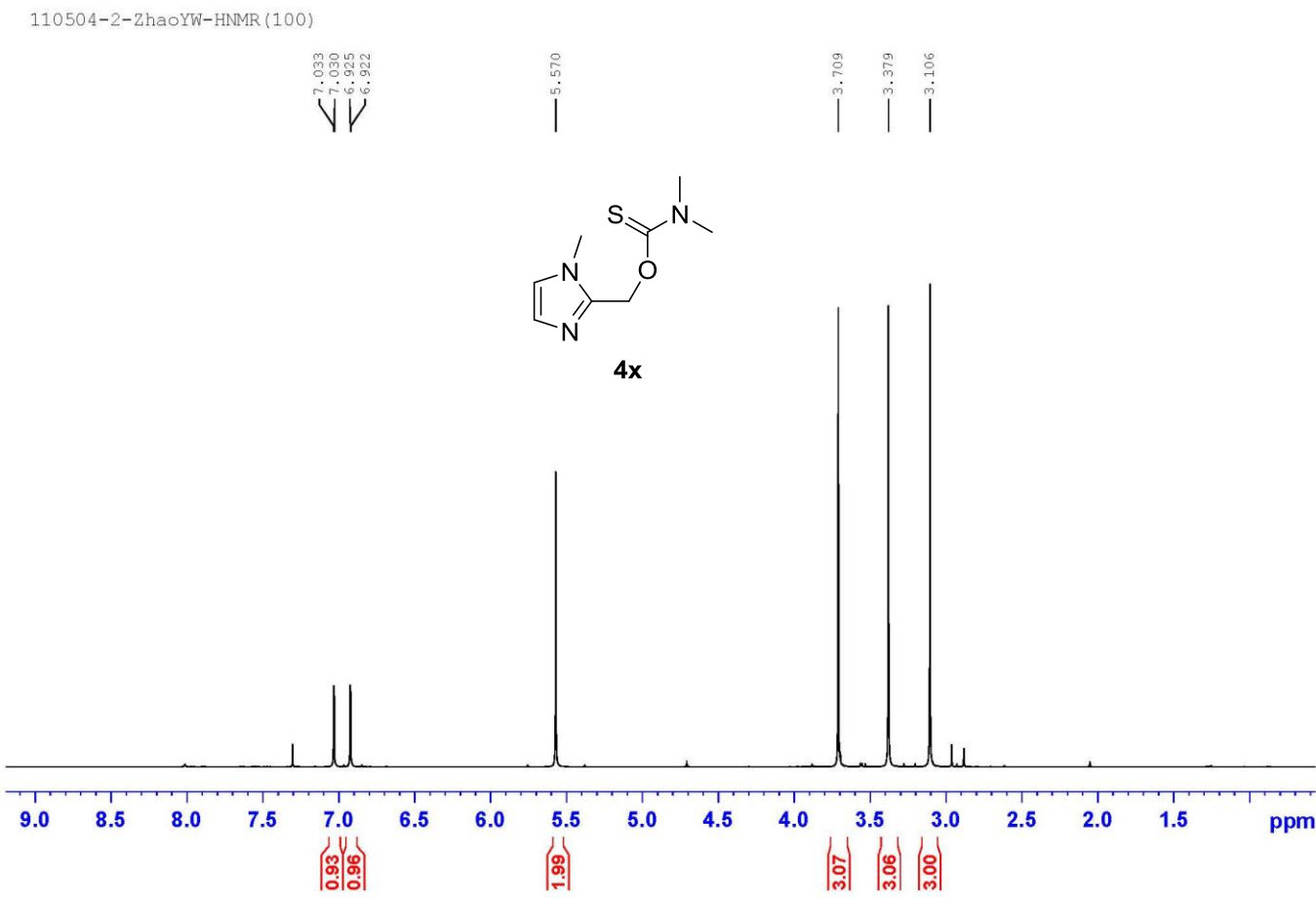


111104-2-ZYW-HNMR

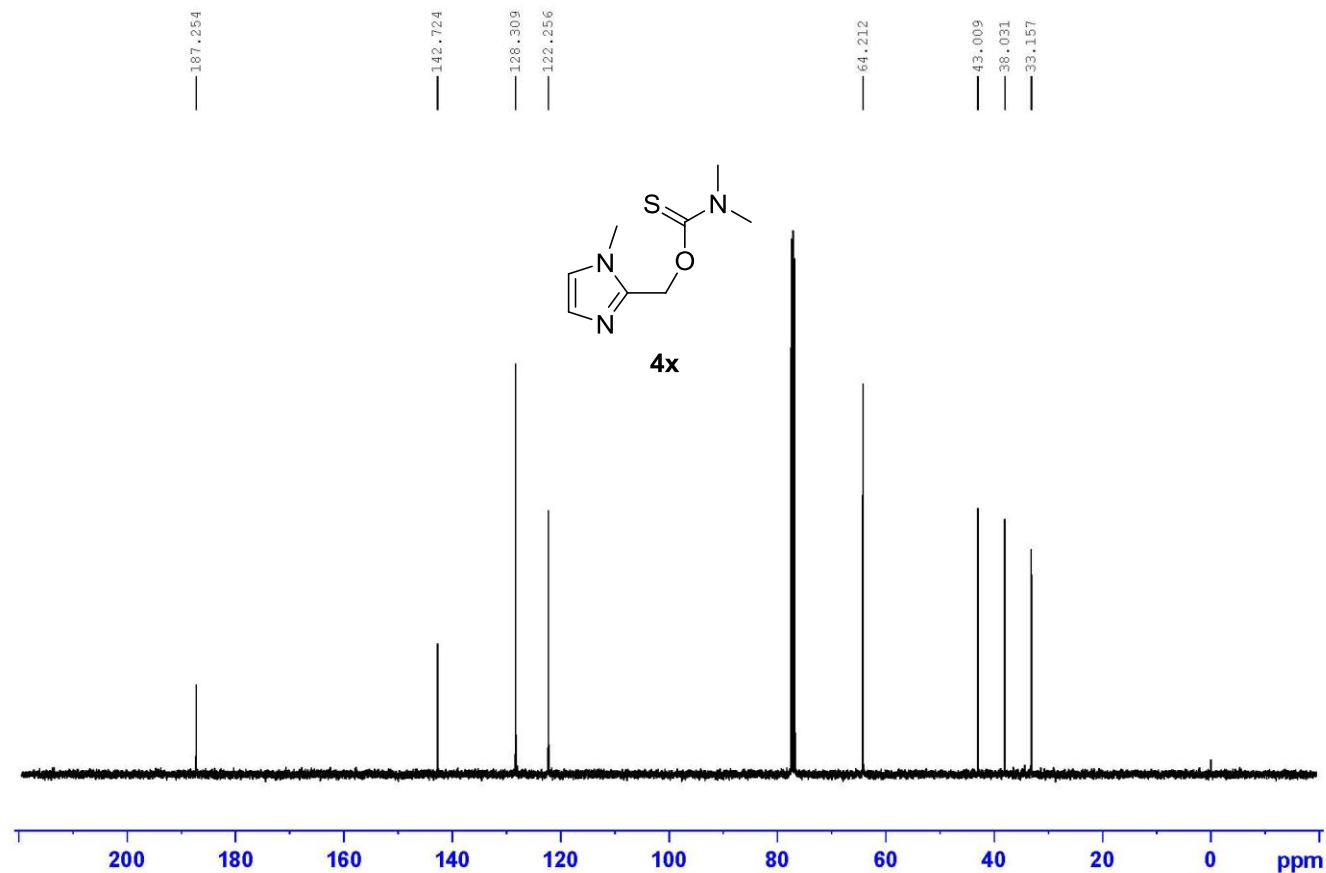


111104-2-ZYW-CNMR



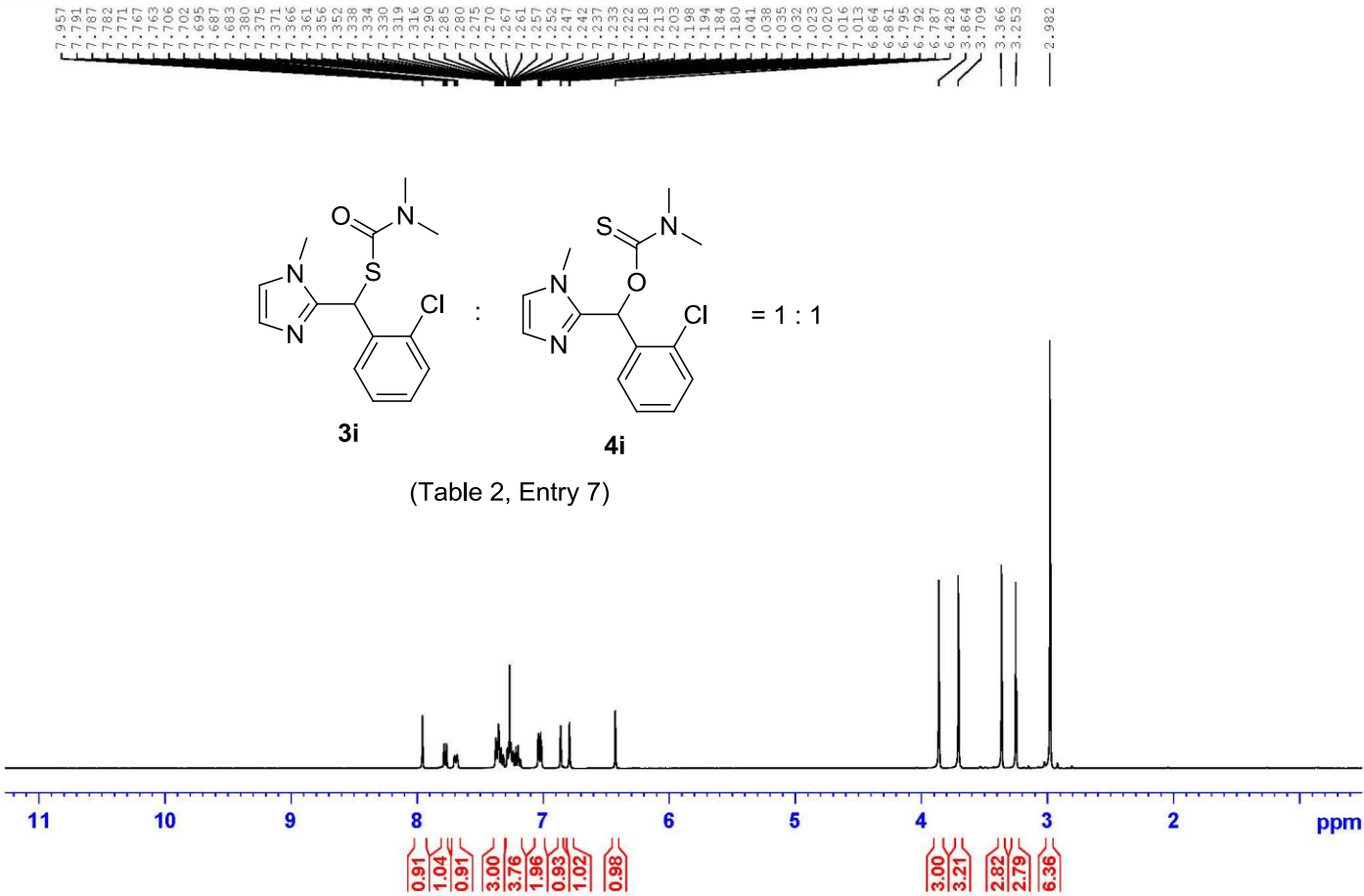


110504-2-ZhaoYW-CNMR(101)

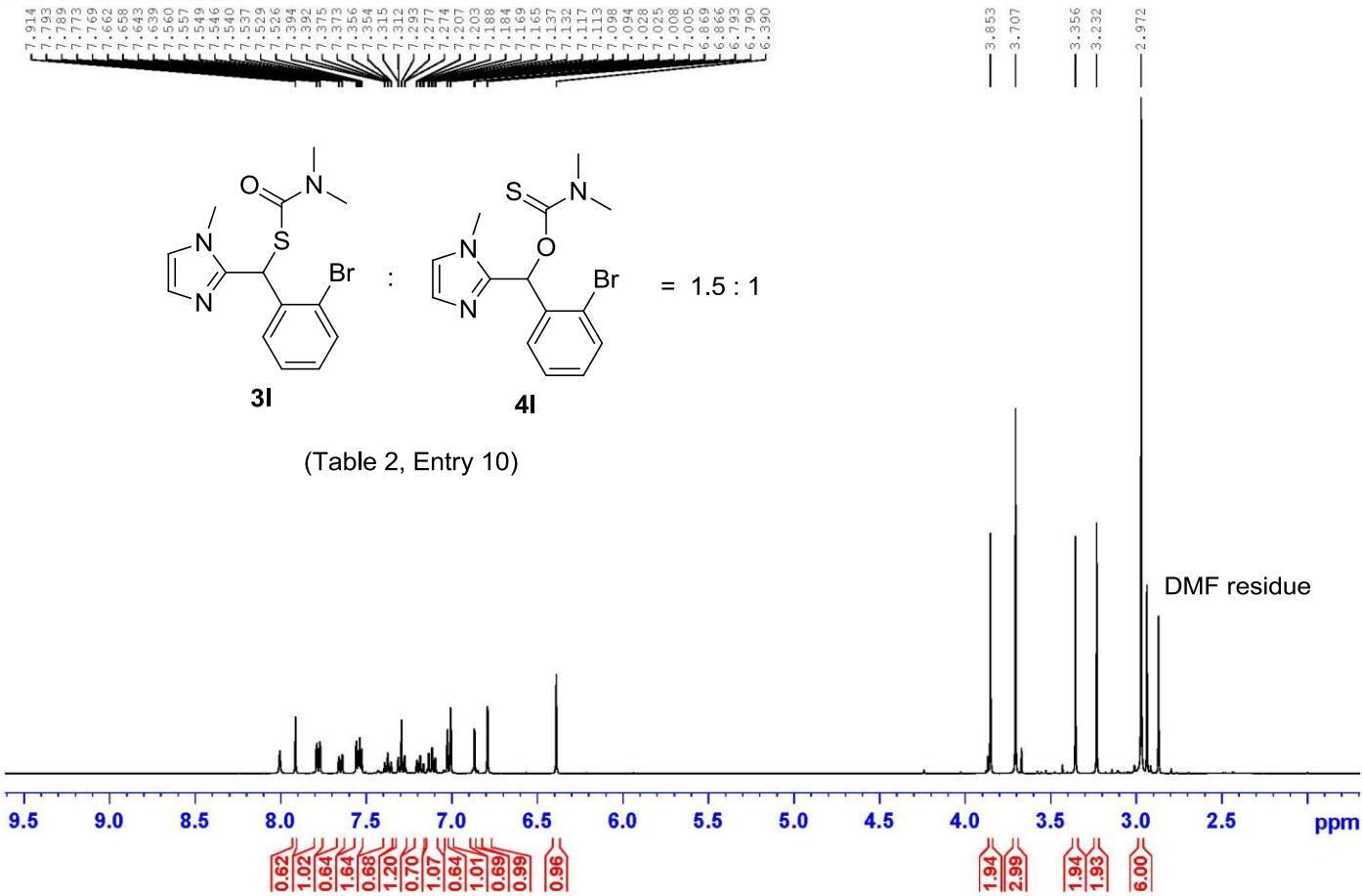




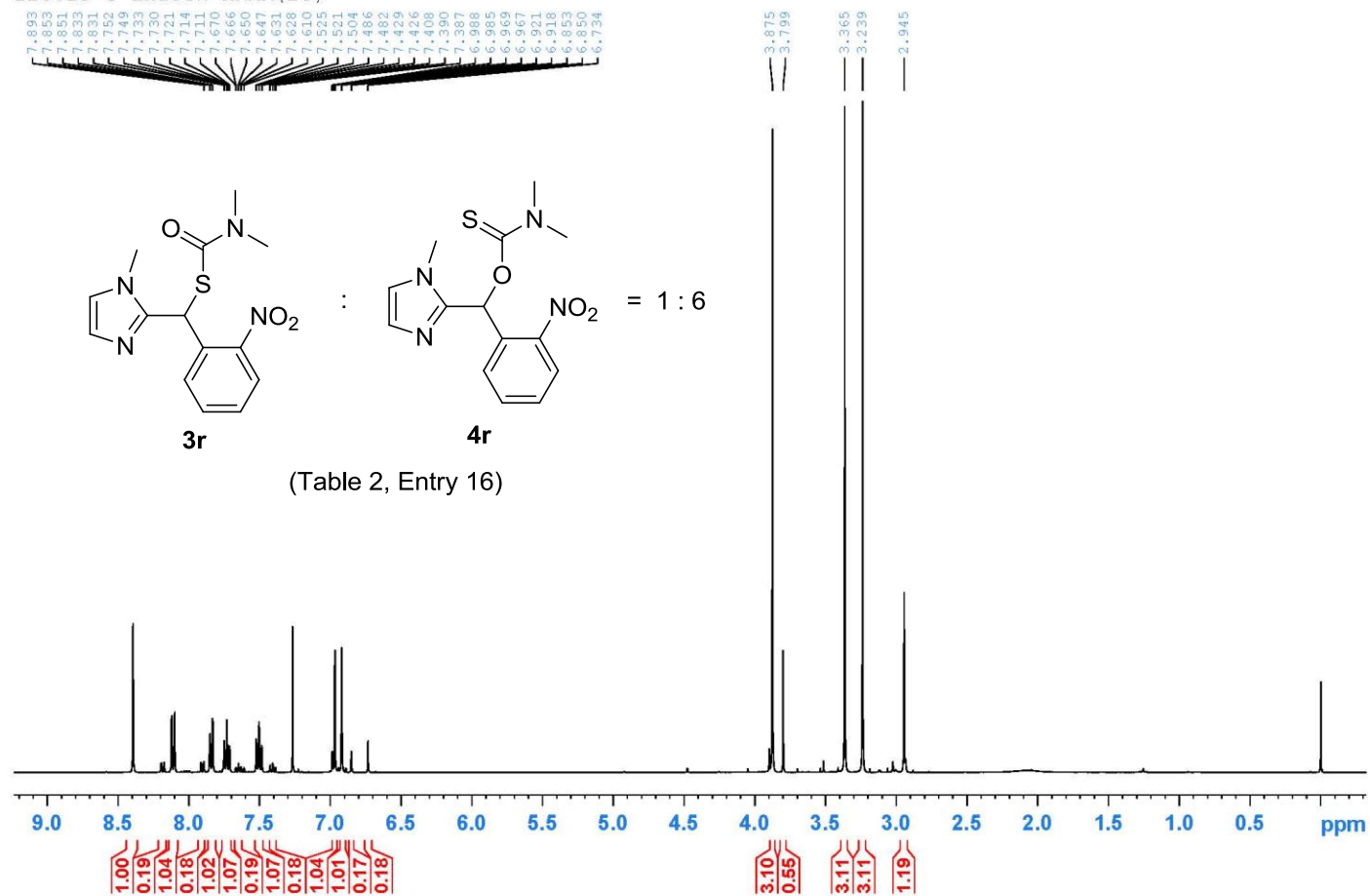
110826-4-ZhaoYW-HNMR(11)



110708-ZYW-10-HNMR



110819-3-ZhaoYW-HNMR (25)



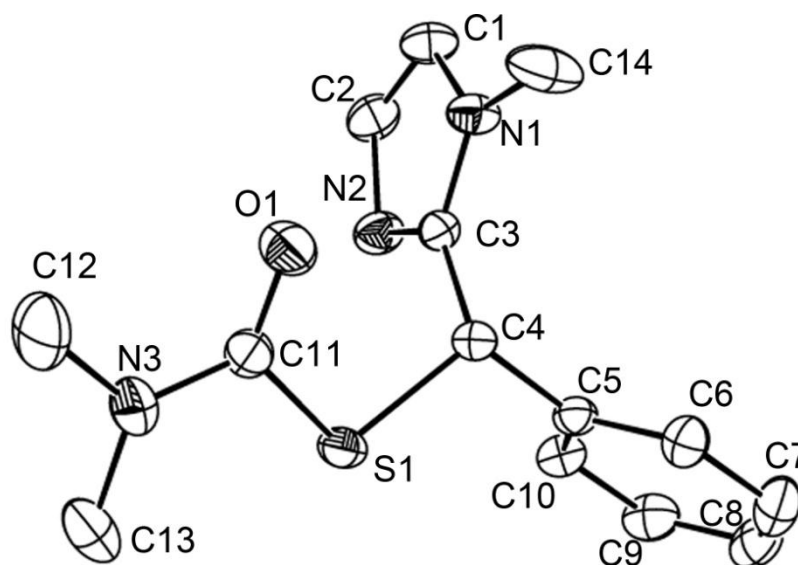


Figure S1. ORTEP illustration for **2a** (hydrogen atoms were omitted for clarity).

**CCDC-880883** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

Bond precision: C-C = 0.0022 Å Wavelength=0.71073  
 Cell: a=8.3769(9) b=12.9848(13) c=13.7325(14)  
 alpha=90 beta=90.834(1) gamma=90  
 Temperature: 296 K  
 Calculated Reported  
 Volume 1493.6(3) 1493.6(3)  
 Space group P 21/n P2(1)/n  
 Hall group -P 2yn ?  
 Moiety formula C14 H17 N3 O S ?  
 Sum formula C14 H17 N3 O S C14 H17 N3 O S  
 Mr 275.38 275.37  
 Dx, g cm<sup>-3</sup> 1.225 1.225  
 Z 4 4  
 Mu (mm<sup>-1</sup>) 0.213 0.213  
 F000 584.0 584.0  
 F000' 584.68  
 h, k, lmax 9, 15, 16 9, 15, 16  
 Nref 2632 2610  
 Tmin, Tmax 0.950, 0.958 0.920, 0.959  
 Tmin' 0.918  
 Correction method= MULTI-SCAN  
 Data completeness= 0.992 Theta(max)= 25.000  
 R(reflections)= 0.0369( 2305) wR2(reflections)= 0.1360( 2610)  
 S = 1.052 Npar= 175