

# **Selectively Actinide-Catalyzed Tandem Proton-Transfer Esterification of Aldehydes with Alcohols for the Production of Asymmetric Esters**

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## Experimental section

### General considerations

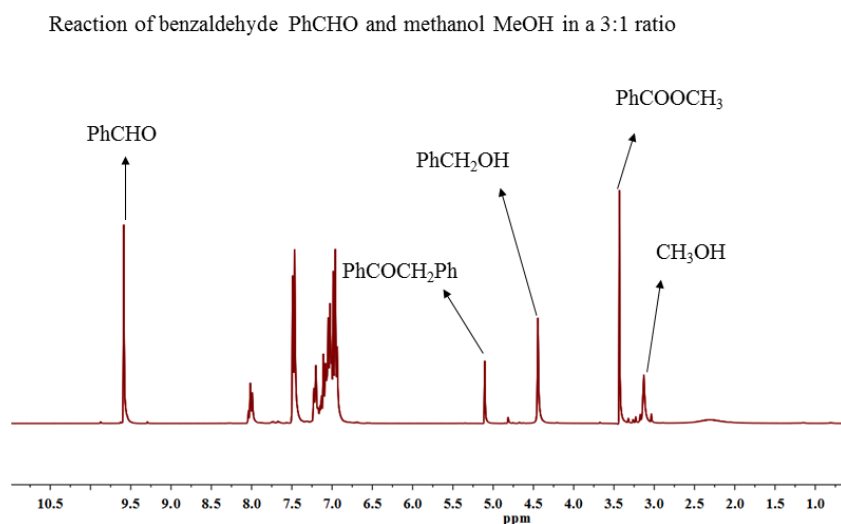
All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware or *J*-Young Teflon valve-sealed NMR tubes on a dual manifold Schlenk line interfaced to a high vacuum ( $10^{-5}$  Torr) line, or in a nitrogen-filled Innovative Technologies glovebox with a medium-capacity recirculator (1 – 2 ppm of O<sub>2</sub>). Argon and nitrogen were purified by passage through MnO oxygen-removal column and a Davison 4Å molecular sieve column. Hydrocarbon solvents benzene-*d*<sup>6</sup> (Cambridge Isotopes), toluene (Bio-Lab), were distilled under vacuum from Na/K alloy. Liquid aldehydes were distilled over sodium bicarbonate and stored in a glovebox prior to use, solid aldehydes were recrystallized twice and then dried for 12 h on a high vacuum line ( $10^{-5}$  Torr) and stored in a glovebox prior to use. Methanol, ethanol, isopropanol, *tert*-butanol, benzyl alcohol was dried using sodium (Na) metal (or CaH<sub>2</sub>), distilled, and stored over 4 Å molecular sieves. The actinide complexes [(Me<sub>3</sub>Si)<sub>2</sub>N]<sub>2</sub>An[ $\kappa^2$ -(*N,C*)-CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>2</sub>N(SiMe<sub>3</sub>)] (An = Th (**1**), U(**2**)) and U[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> (**3**) were prepared according to published procedures.<sup>1</sup> All the aforementioned reagents were stored in an inert atmosphere glovebox prior to use. *O*-deuterated methanol was purchased from Sigma Aldrich, and dried according the above procedure, and storing over 4 Å molecular sieves. Deuterated benzylaldehyde, PhCDO, was prepared according to previous reports, storing over 4 Å molecular sieves after being dried.<sup>2</sup>

NMR spectra were recorded on Bruker Avance 300, Bruker Avance III 400 spectrometers on crude reaction mixtures. Chemical shifts for <sup>1</sup>H and <sup>13</sup>C NMR are referenced to internal protiosolvent and reported relative to tetramethylsilane.

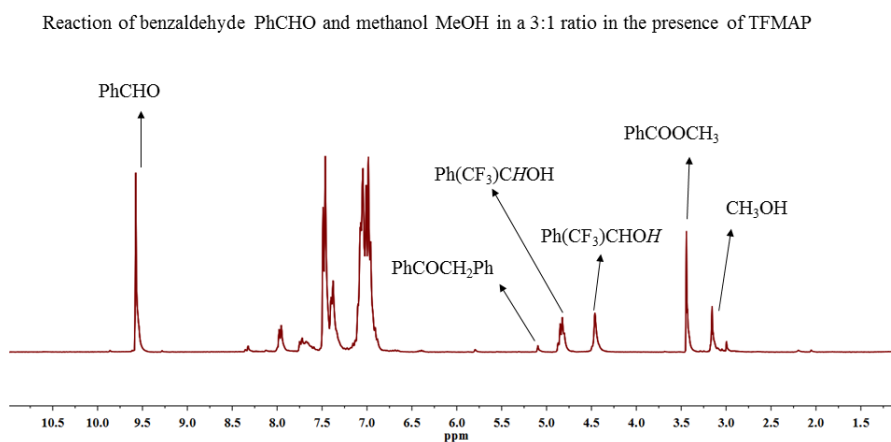
### General procedures for proton transfer esterification process

In a typical experiment, into a J. Young Teflon sealed NMR tube was added aldehyde (1.044 mmol) and alcohol (0.348 mmol) ( $\alpha,\alpha,\alpha$ -trifluoromethylacetophenone was added if necessary), followed by adding desired amount of catalyst (7  $\mu$ mol) in C<sub>6</sub>D<sub>6</sub>. Samples were then sealed and placed in an oil bath preheated to 70 °C, and the

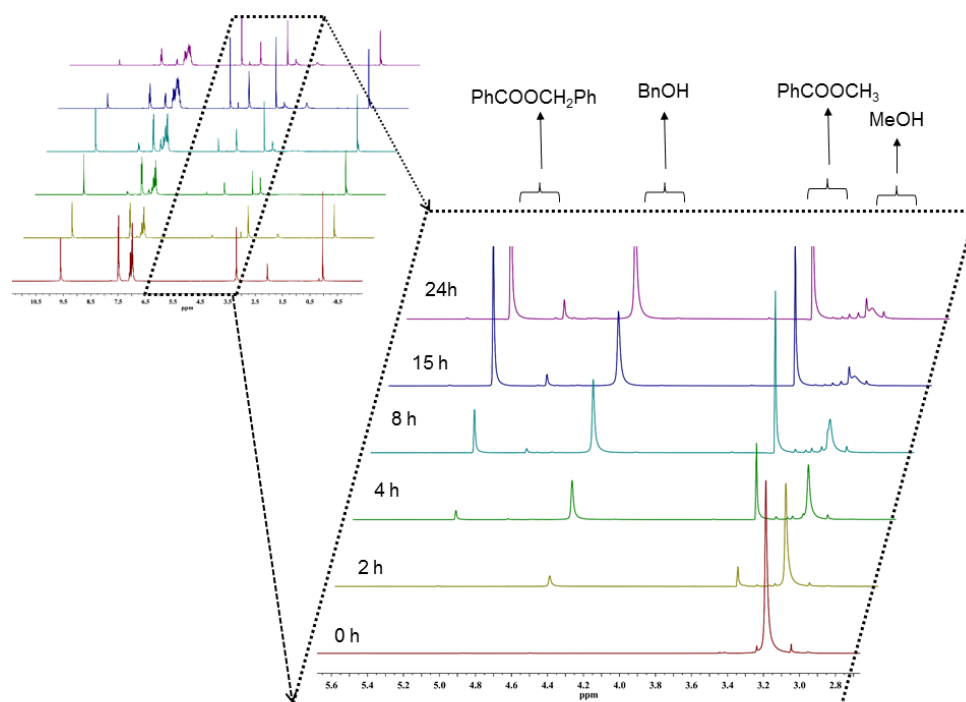
reaction progress monitored at regular intervals using  $^1\text{H}$  NMR spectroscopy for up to 24 hours. The yield was calculated from the ratio of esters and alcohols from the crude  $^1\text{H}$  NMR spectra (see examples in Figure S1). After completion of the reaction, the pure product was obtained by flash column chromatography on silica gel (20:1) and compared with previous reports.



**Figure S1.** Crude  $^1\text{H}$  NMR spectra of the reaction between PhCHO and MeOH (3:1).

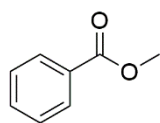


**Figure S2.** Crude  $^1\text{H}$  NMR spectra of the reaction between PhCHO and MeOH (3:1) in the presence of TFMAP

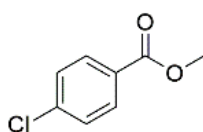


**Figure S3.** Reaction progress of the reaction between PhCHO and MeOH (3:1).

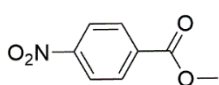
#### Characterization data



**Methyl benzoate<sup>3</sup>:** reaction of benzaldehyde (1.044mmol, 106.4  $\mu$ L) with methanol (0.348mmol, 14.1 $\mu$ L) was carried out following the general procedure described above.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.13 – 7.86 (m, 2H,  $H_{\text{Ar}}$ ), 7.67 – 7.33 (m, 3H,  $H_{\text{Ar}}$ ), 3.94 (s, 3H,  $\text{OCH}_3$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  167.13, 132.92, 130.13, 129.57, 128.36, 52.12. MS (APCI):  $m/z$  137.0607( $\text{M}+\text{H}$ )\*.

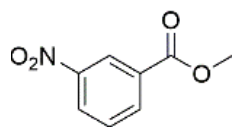


**Methyl 4-chlorobenzoate<sup>4</sup>:** reaction of 4-chlorobenzaldehyde (1.044mmol, 146.8mg) with methanol (0.348mmol, 14.1 $\mu$ L) was carried out following the general procedure described above.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 – 7.84 (m, 2H,  $H_{\text{Ar}}$ ), 7.50 – 7.31 (m, 2H,  $H_{\text{Ar}}$ ), 3.89 (s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  166.15, 139.26, 130.86, 128.61, 128.45, 51.92. MS (APCI):  $m/z$  171.0204 ( $\text{M}+\text{H}$ )\*.

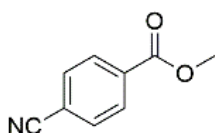


**Methyl 4-nitrobenzoate<sup>5</sup>:** reaction of 4-nitrobenzaldehyde (1.044mmol, 157.8mg) with methanol (0.348mmol, 14.1 $\mu$ L) was carried out following the general procedure described above.  $^1\text{H}$  NMR (300 MHz,

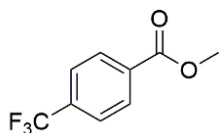
CDCl<sub>3</sub>)  $\delta$  8.41 – 8.22 (m, 2H, *H*<sub>Ar</sub>), 8.17 (m, 2H, *H*<sub>Ar</sub>), 3.98 – 3.86 (m, 3H, *CH*<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  165.07, 150.35, 135.35, 130.60, 123.44, 52.74. MS (APCI): *m/z* 182.0476(M+H)\*.



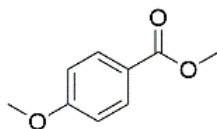
**Methyl 3-nitrobenzoate**<sup>6</sup>: reaction of 3-nitrobenzaldehyde (1.044mmol, 157.8mg) with methanol (0.348mmol, 14.1 $\mu$ L) was carried out following the general procedure described above. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.91 – 8.76 (m, 1H, *H*<sub>Ar</sub>), 8.50 – 8.25 (m, 2H, *H*<sub>Ar</sub>), 7.74 – 7.50 (m, 1H, *H*<sub>Ar</sub>), 3.98 (s, 3H, *CH*<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  164.86, 148.14, 135.18, 131.73, 129.54, 127.30, 124.51, 52.72. MS (APCI): *m/z* 182.0411(M+H)\*.



**Methyl 4-cyanobenzoate**<sup>5</sup>: reaction of 4-cyanobenzaldehyde (1.044mmol, 136.9mg) with methanol (0.348mmol, 14.1 $\mu$ L) was carried out following the general procedure described above. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.15 – 8.00 (m, 2H, *H*<sub>Ar</sub>), 7.80 – 7.55 (m, 2H, *H*<sub>Ar</sub>), 3.93 (s, 3H, *CH*<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  165.33, 133.79, 132.12, 129.99, 117.87, 116.27, 52.64. MS (APCI): *m/z* 162.0563 (M+H)\*.

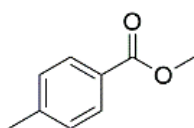


**Methyl 4-trifluoromethylbenzoate**<sup>7</sup>: reaction of 4-trifluorobenzaldehyde (1.044mmol, 140.0 $\mu$ L) with methanol (0.348mmol, 14.1 $\mu$ L) was carried out following the general procedure described above. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.14 (d, *J* = 8.1 Hz, 1H, *H*<sub>Ar</sub>), 7.69 (d, *J* = 8.1 Hz, 1H, *H*<sub>Ar</sub>), 3.94 (s, 3H, *CH*<sub>3</sub>). MS (APCI): *m/z* 205.0433(M+H)\*.

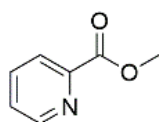


**Methyl anisate**<sup>5</sup>: reaction of 4-anisaldehyde (1.044mmol, 126.8 $\mu$ L) with methanol (0.348mmol, 14.1 $\mu$ L) was carried out following the general procedure described above. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.03 – 7.87 (m, 2H, *H*<sub>Ar</sub>), 6.95 – 6.73 (m, 2H, *H*<sub>Ar</sub>), 3.87 – 3.86 (m, 3H, *CH*<sub>3</sub>), 3.85 – 3.83 (m, 2H, *CH*<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  166.78, 163.22, 131.48, 122.53, 113.32, 55.21, 51.71. MS (APCI): *m/z* 166.01 (M+H)\*.

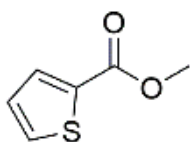
**Methyl 4-methylbenzoate**<sup>5</sup>: reaction of 4-methylbenzaldehyde (1.044mmol, 123.1  $\mu$ L) with methanol (0.348mmol, 14.1 $\mu$ L) was carried out following the general procedure



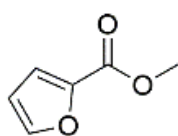
described above.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 – 7.84 (m, 2H,  $H_{\text{Ar}}$ ), 7.19 – 7.14 (m, 2H,  $H_{\text{Ar}}$ ), 3.87 (s, 3H,  $\text{CH}_3$ ), 2.38 (s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  167.10, 143.46, 129.48, 128.97, 127.28, 51.39, 21.29. MS (APCI):  $m/z$  151.0758 ( $\text{M}+\text{H}$ )\*.



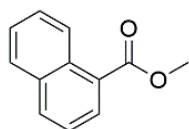
**Methyl picolinate**<sup>8</sup>: reaction of 2-pyridinecarboxaldehyde (1.044mmol, 99.3  $\mu\text{L}$ ) with methanol (0.348mmol, 14.1  $\mu\text{L}$ ) was carried out following the general procedure described above.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.81 – 8.63 (m, 1H,  $H_{\text{Ar}}$ ), 8.28 – 7.96 (m, 1H,  $H_{\text{Ar}}$ ), 7.88 – 7.64 (m, 1H,  $H_{\text{Ar}}$ ), 7.54 – 7.36 (m, 1H,  $H_{\text{Ar}}$ ), 3.99 (s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  165.59, 149.69, 147.82, 136.92, 126.83, 125.01, 52.78. MS (APCI):  $m/z$  138.0572 ( $\text{M}+\text{H}$ )\*.



**Methyl thienoate**<sup>9</sup>: reaction of 2-thenaldehyde (1.044mmol, 97.6  $\mu\text{L}$ ) with methanol (0.348mmol, 14.1  $\mu\text{L}$ ) was carried out following the general procedure described above.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80 – 7.77 (m, 1H,  $H_{\text{Ar}}$ ), 7.55 – 7.52 (m, 1H,  $H_{\text{Ar}}$ ), 7.11 – 7.06 (m, 1H,  $H_{\text{Ar}}$ ), 3.87 (s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  162.83, 133.71, 133.38, 132.22, 127.65, 51.96. MS (APCI):  $m/z$  143.0174 ( $\text{M}+\text{H}$ )\*.

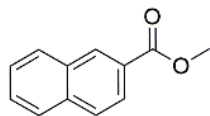


**Methyl 2-furoate**<sup>9</sup>: reaction of 2-furaldehyde (1.044mmol, 87  $\mu\text{L}$ ) with methanol (0.348mmol, 14.1  $\mu\text{L}$ ) was carried out following the general procedure described above.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 – 7.53 (m, 1H,  $H_{\text{Ar}}$ ), 7.19 – 7.13 (m, 1H,  $H_{\text{Ar}}$ ), 6.54 – 6.46 (m, 1H,  $H_{\text{Ar}}$ ), 3.88 (s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  158.95, 146.15, 143.41, 117.80, 111.71, 51.79. MS (APCI):  $m/z$  127.0411 ( $\text{M}+\text{H}$ )\*.

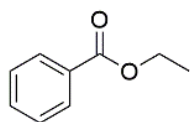


**Methyl naphthalene-1-carboxylate**<sup>5</sup>: reaction of 1-naphthaldehyde (1.044mmol, 141.8  $\mu\text{L}$ ) with methanol (0.348mmol, 14.1  $\mu\text{L}$ ) was carried out following the general procedure described above.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.92 – 8.83 (m, 1H,  $H_{\text{Ar}}$ ), 8.20 – 8.11 (m, 1H,  $H_{\text{Ar}}$ ), 8.01 (d,  $J$  = 8.2 Hz, 1H,  $H_{\text{Ar}}$ ), 7.91 – 7.80 (m, 1H,  $H_{\text{Ar}}$ ), 7.64 – 7.56 (m, 1H,  $H_{\text{Ar}}$ ), 7.56 – 7.43 (m, 2H,  $H_{\text{Ar}}$ ), 3.99 (s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  167.95, 133.71, 133.27,

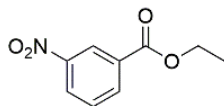
131.20, 130.11, 128.43, 127.66, 126.95, 126.10, 125.68, 124.39, 51.71. MS (APCI):  $m/z$  187.0838 (M+H)\*.



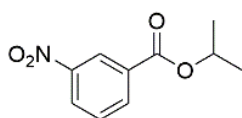
**Methyl naphthalene-2-carboxylate**<sup>5</sup>: reaction of 2-naphthaldehyde (1.044mmol, 163.5mg) with methanol (0.348mmol, 14.1 $\mu$ L) was carried out following the general procedure described above. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.60 (s, 1H, *H*<sub>Ar</sub>), 8.05 (d, *J* = 8.6 Hz, 1H, *H*<sub>Ar</sub>), 7.98 – 7.91 (m, 1H, *H*<sub>Ar</sub>), 7.90 – 7.82 (m, 2H, *H*<sub>Ar</sub>), 7.61 – 7.48 (m, 2H, *H*<sub>Ar</sub>), 3.97 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  167.17, 135.39, 132.36, 130.96, 129.25, 128.13, 128.05, 127.65, 127.26, 126.53, 125.11, 52.03. MS (APCI):  $m/z$  187.0762 (M+H)\*.



**Methyl benzoate**<sup>9</sup>: reaction of benzaldehyde (1.044mmol, 106.4  $\mu$ L) with ethanol (0.348mmol, 20.3  $\mu$ L) was carried out following the general procedure described above. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.07 – 7.95 (m, 2H, *H*<sub>Ar</sub>), 7.57 – 7.45 (m, 1H, *H*<sub>Ar</sub>), 7.45 – 7.34 (m, 2H, *H*<sub>Ar</sub>), 4.51 – 4.19 (q, *J* = 7.2 Hz, 2H, CH<sub>2</sub>), 1.36 (t, *J* = 7.2 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  166.43, 132.68, 130.37, 129.22, 128.07, 60.57, 14.19. MS (APCI):  $m/z$  151.0748 (M+H)\*.

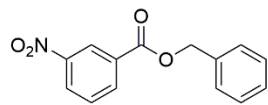


**Ethyl 3-nitrobenzoate**<sup>10</sup>: reaction of 3-nitrobenzaldehyde (1.044mmol, 157.8mg) with ethanol (0.348mmol, 20.3 $\mu$ L) was carried out following the general procedure described above. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.84 – 8.70 (m, 1H, *H*<sub>Ar</sub>), 8.39 – 8.17 (m, 2H, *H*<sub>Ar</sub>), 7.64 – 7.46 (m, 1H, *H*<sub>Ar</sub>), 4.35 (q, *J* = 7.1 Hz, 2H, CH<sub>2</sub>), 1.34 (d, *J* = 7.1 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  161.77, 148.12, 135.17, 131.97, 129.49, 127.12, 124.23, 61.46, 13.78. MS (APCI):  $m/z$  195.0291.

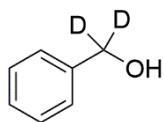


**Isopropyl 3-nitrobenzoate**<sup>10</sup>: reaction of 3-nitrobenzaldehyde (1.044mmol, 157.8mg) with isopropanol (0.348mmol, 26.6 $\mu$ L) was carried out following the general procedure described above. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.90 – 8.78 (m, 1H, *H*<sub>Ar</sub>), 8.45 – 8.30 (m, 2H, *H*<sub>Ar</sub>), 7.67 – 7.56 (m, 1H, *H*<sub>Ar</sub>), 5.28 (hept, *J* = 6.3 Hz, 1H, CH), 1.39 (d, *J* = 6.3 Hz, 6H, CH<sub>3</sub>). <sup>13</sup>C

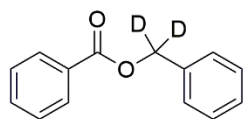
NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  191.69, 162.21, 149.45, 135.23, 132.55, 129.38, 126.98, 124.35, 69.38, 21.76. MS (APCI):  $m/z$  209.0431.



**Phenylmethyl 3-nitrobenzoate**<sup>10</sup> : reaction of 3-nitro benzaldehyde (1.044mmol, 157.8mg) with benzyl alcohol (0.348mmol, 36.05 $\mu$ L) was carried out following the general procedure described above. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.91 – 8.82 (m, 1H), 8.54 – 8.26 (m, 2H), 7.63 (t,  $J$  = 7.7 Hz, 1H), 7.48 – 7.34 (m, 5H), 5.40 (s, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  164.21, 148.20, 135.26, 135.14, 131.81, 129.52, 128.63, 128.54, 128.37, 127.37, 124.57, 67.51. MS (APCI):  $m/z$  257.0742.



**Benzyl alcohol-*d*<sub>2</sub>**<sup>11</sup>: reaction of benzaldehyde-*d* (1.044mmol, 110.2mg) with methanol (0.348mmol, 14.1 $\mu$ L) was carried out following the general procedure described above. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.35 (d, 4H,  $H_{Ar}$ ), 7.32 – 7.25 (m, 1H,  $H_{Ar}$ ), 1.65 (s, 1H, OH). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  140.68, 128.52, 127.51, 126.87, 64.95.



**Benzyl benzoate-*d*<sub>2</sub>**: reaction of benzaldehyde-*d* (1.044mmol, 110.2mg) with methanol (0.348mmol, 14.1 $\mu$ L) was carried out following the general procedure described above. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.07 (d,  $J$  = 7.7 Hz, 2H), 7.54 (t,  $J$  = 7.1 Hz, 1H), 7.49 – 7.28 (m, 7H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  166.31, 135.82, 132.90, 130.12, 129.59, 128.48, 128.25, 128.14, 128.09, 65.83. MS (APCI):  $m/z$  214.1290.

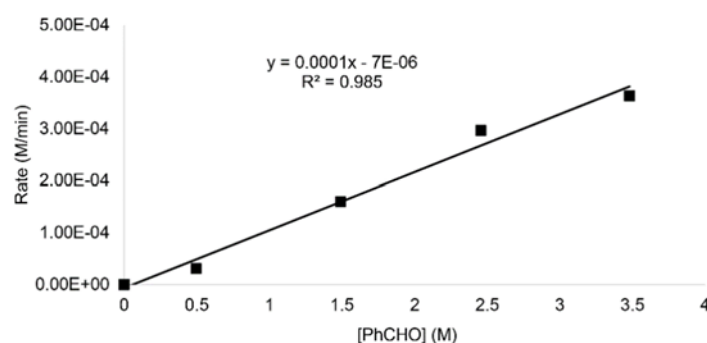
### Kinetic studies

All the kinetic experiments were done in a similar method. In a J. Young NMR tube, typical amount of precatalyst **1** (3 – 14  $\mu$ mol), PhCHO (0.348 - 2.1mmol), CH<sub>3</sub>OH (0.174 – 1.044) and C<sub>6</sub>D<sub>6</sub> was added in the glove box and then the tube was sealed. Take the tube out of the glove box and freeze it in ice bath until the <sup>1</sup>H NMR experiment began. All the experiments were done by changing one substrate or catalyst while keeping the other reagents constant, and the data was collected every five minutes up to six hours. The product concentrations were measured by the area ratio of *methyl* group at 3.08 ppm and 3.42 ppm, which were assigned to the starting material MeOH

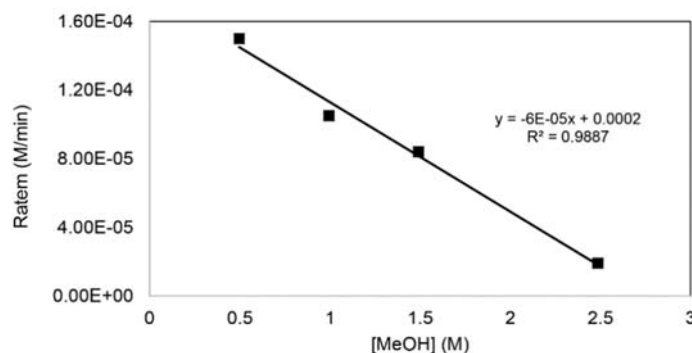


and ester product PhCOOMe respectively. Reaction rates were determined by least-square fit of product concentration versus time, and the plots were shown in Figures S4-6.

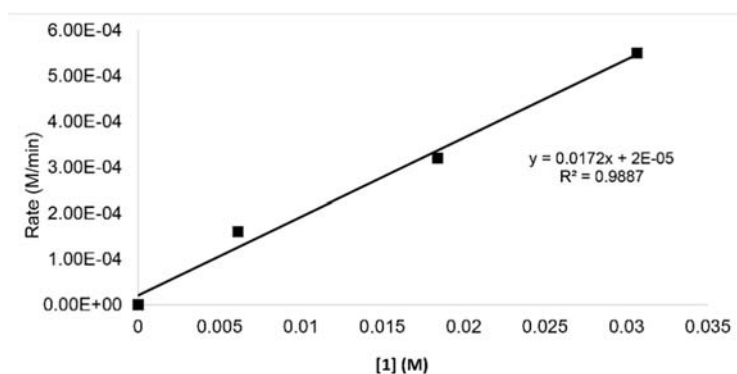
Activation parameters including enthalpy ( $\Delta H^\ddagger$ ), entropy ( $\Delta S^\ddagger$ ) and activation energy ( $E_a$ ) were calculated from kinetic data using Eyring and Arrhenius plots. In a typical sample, the J. Young tube was loaded with desired amount of precatalyst **1**, PhCHO, CH<sub>3</sub>OH, C<sub>6</sub>D<sub>6</sub> and sealed. Then the sample was inserted into Bruker Avance 300 spectrometer which had been previously set to the desired temperature. The data was collected every one minute up to six hours. Reaction rates were determined by the least square fit of product concentration versus time, and Eyring and Arrhenius plots were shown in Figures S7-8. Enthalpy ( $\Delta H^\ddagger$ ), entropy ( $\Delta S^\ddagger$ ) and activation energy ( $E_a$ ) were calculated from the slope and intercept of the least-square fit.



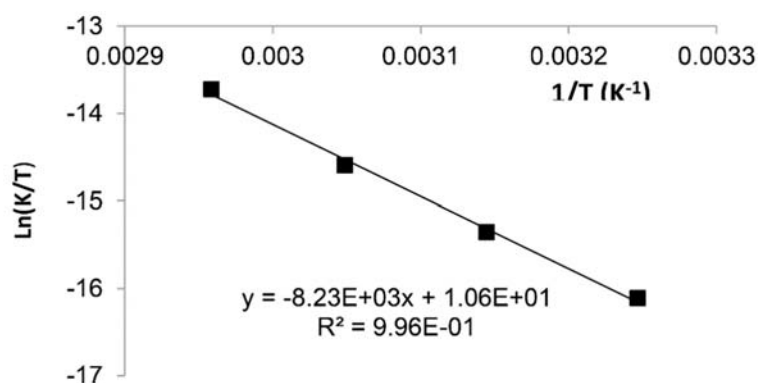
**Figure S4.** Plot of reaction rate versus concentration of PhCHO by complex **1**.



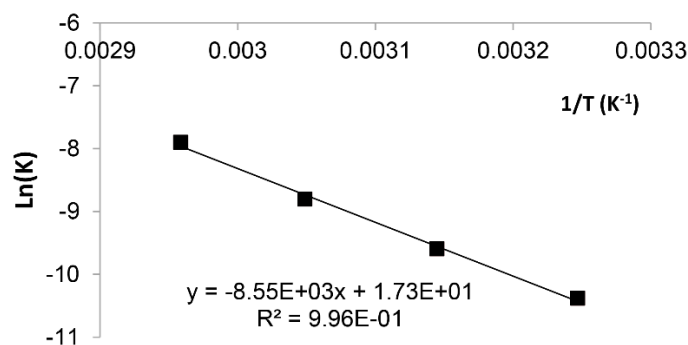
**Figure S5.** Plot of reaction rate versus concentration of MeOH by complex **1**.



**Figure S6.** Plot of reaction rate versus concentration of complex **1**.



**Figure S7.** Eyring plot for the reaction of PHCO and MeOH using complex **1**.

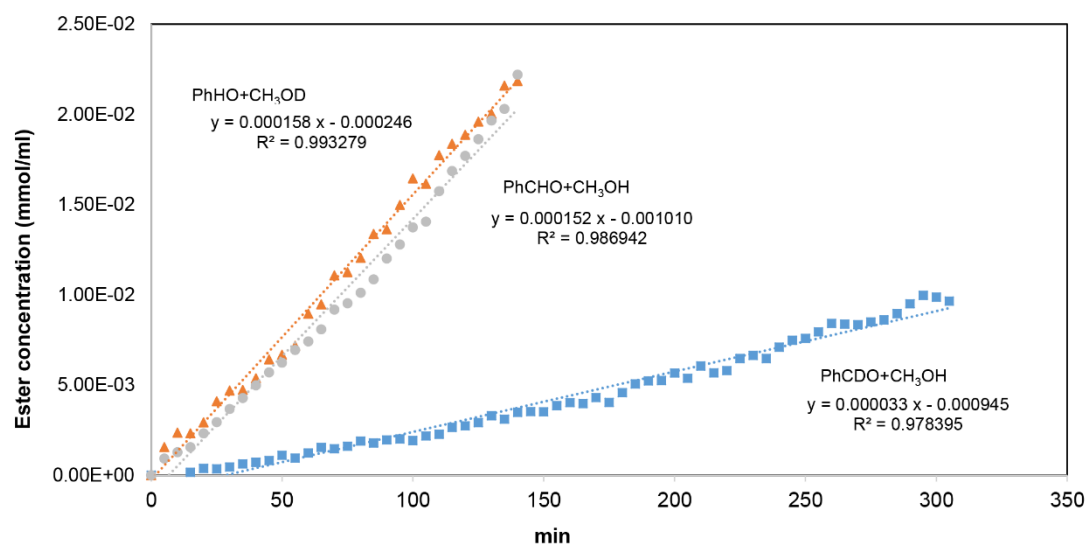


**Figure S8.** Arrhenius plot for the reaction of PHCHO and MeOH using complex **1**.

### Deuterium labeling studies.

In a J. Young NMR tube, typical amount of precatalyst **1** (7  $\mu\text{mol}$ ), PhCHO (or PhCDO, 1.044mmol), CH<sub>3</sub>OH (MeOD, 1.044 mmol) and C<sub>6</sub>D<sub>6</sub> was added in the glove box and then the tube was sealed. Take the tube out of the glove box and freeze it in ice bath until the <sup>1</sup>H NMR experiment began. All the experiments were done by changing

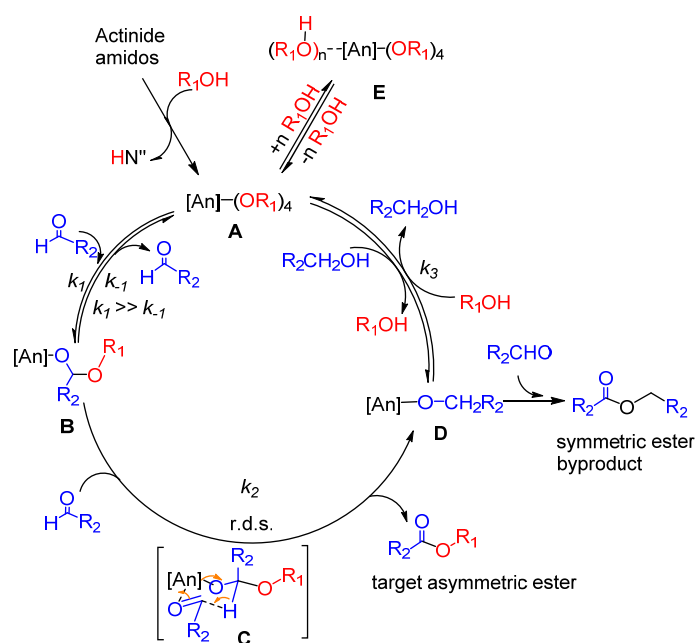
one substrate or catalyst while keeping the other reagents constant, and the data was collected every five minutes up to six hours. The reaction progresses were shown in Figure S9.



**Figure S9.** Reaction progress of the reaction of precatalyst **1**, PhCHO (or PhCDO), CH<sub>3</sub>OH (MeOD).

### Discussion of kinetic rate law

According to the kinetic and thermodynamic data, the following mechanism is proposed:



Deuterium labeling studies showed that the hydride transfer through the six-member ring insertion is the turnover limiting step, and the remaining steps of the cycle are rapid ( $k_1, k_3$ ), so the following rate equation can be obtained based on the assumption of a steady-state:

$$\frac{\partial p}{\partial t} = k_2[\mathbf{B}][R_2CHO]$$

$$k_1[\mathbf{A}][R_2CHO] - k_{-1}[\mathbf{B}] - k_2[\mathbf{B}][R_2CHO] = 0$$

Substitution **B** with **A** gives the following equation:

$$\frac{\partial p}{\partial t} = k_2 \frac{k_1[\mathbf{A}][R_2CHO]^2}{k_{-1} + k_2[R_2CHO]}$$

In the formation of species **A**, alcoholysis of actinide amido compounds is rapid and irreversible, however, the equilibrium of alcohol coordination/decoordination to actinide center must be considered,<sup>12</sup> giving the following expression:

$$K_{eq} = \frac{[\mathbf{E}]}{[R_1OH][\mathbf{A}]}$$

From the reaction cycle, it can be found that the sum of active catalysts (**A**) and alcohol-saturated complex (**E**) is the total amount of catalyst loading  $[\text{An}]$  used in the reaction:  $[\mathbf{A}] + [\mathbf{E}] = [\text{An}]$ . After substitution of  $[\mathbf{A}]$  from equilibrium expression into rate equation, the following kinetic rate law is obtained:

$$\frac{\partial p}{\partial t} = k_2 \frac{k_1[\text{An}][R_2CHO]^2}{(1 + K_{eq}[R_1OH])(k_{-1} + k_2[R_2CHO])}$$

From this equation, inverse-first order behavior on  $R_1OH$  and first order dependence on  $[R_2CHO]$  can be concluded if  $K_{eq}[R_1OH]$  is very large and  $k_2[R_2CHO] \gg k_{-1}$ , giving rise to the equation as following:

$$\frac{\partial p}{\partial t} = \frac{k_1}{K_{eq}} \frac{[\text{An}][R_2CHO]}{[R_1OH]} = k'[\text{An}][R_2CHO][R_1OH]^{-1}$$

### **Stoichiometric reactions**

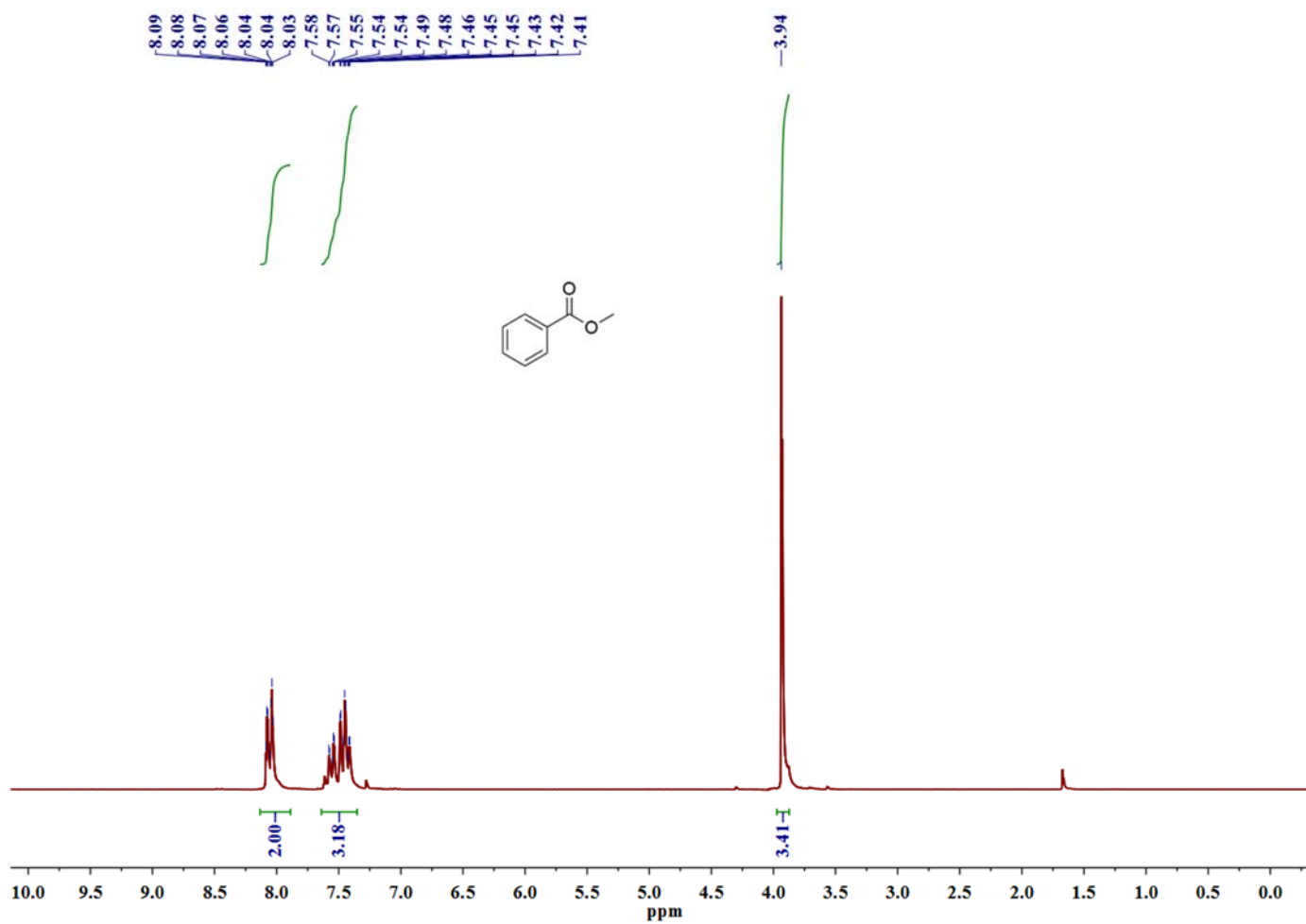
A J. Young NMR tube was loaded with 0.056 mmol complex **1**, 0.56 mmol of MeOH, and 500  $\mu\text{L}$   $\text{C}_6\text{D}_6$ , and then the tube was put into the oil bath which had been previously set to desired temperature (70°C), and monitored by  $^1\text{H}$  NMR spectroscopy.

After 12h, another 0.56 mmol of PhCHO was added, and the reaction was monitored by  $^1\text{H}$  NMR spectroscopy.

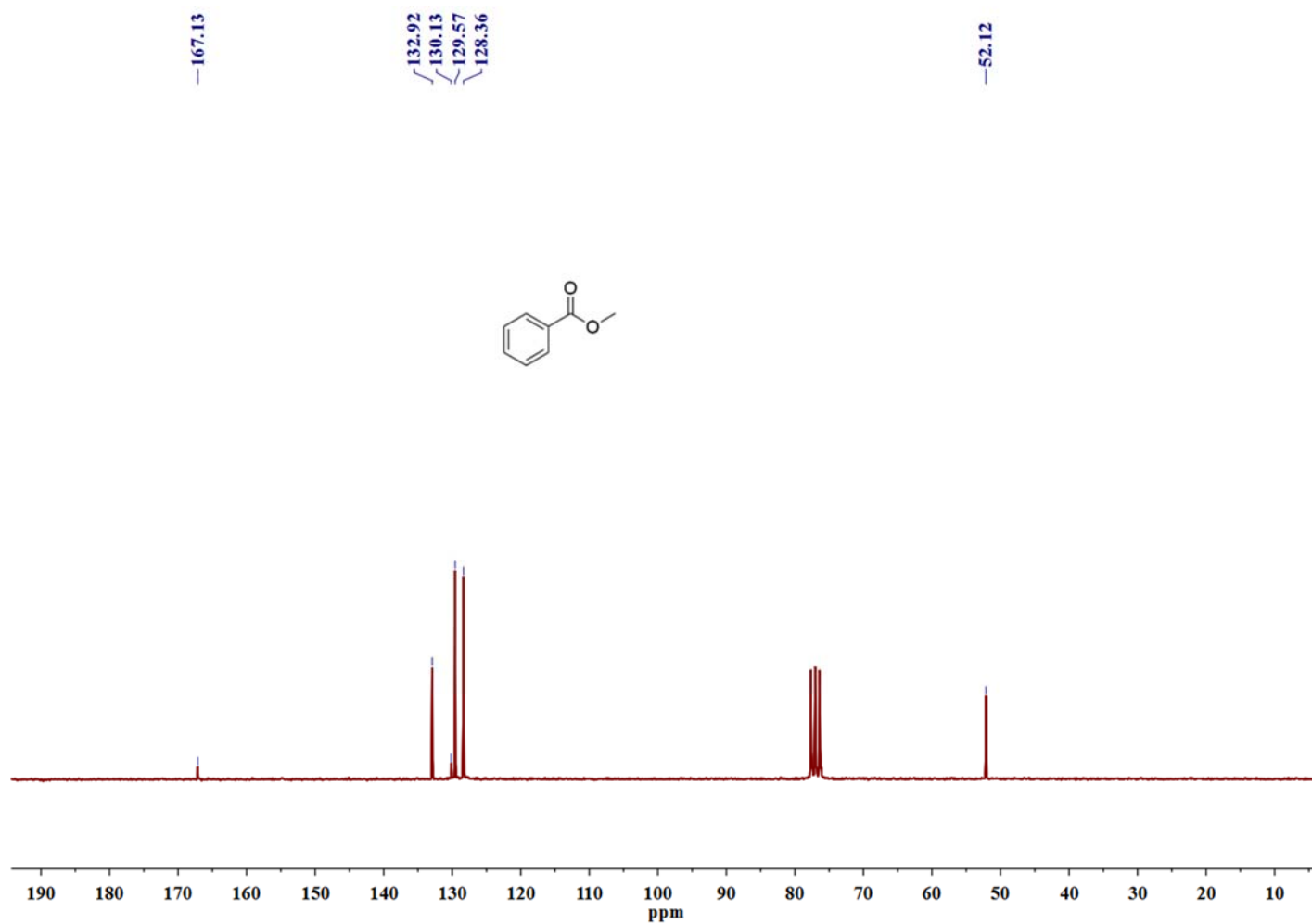
A J. Young NMR tube was loaded with 0.056 mmol complex **1**, 0.56 mmol of PhCHO and 500  $\mu\text{L}$   $\text{C}_6\text{D}_6$ , and then the tube was put into the oil bath which had been previously set to desired temperature ( $70^\circ\text{C}$ ), and monitored by  $^1\text{H}$  NMR spectroscopy. After 12h, another 0.56 mmol of MeOH was added, and the reaction was monitored by  $^1\text{H}$  NMR spectroscopy.

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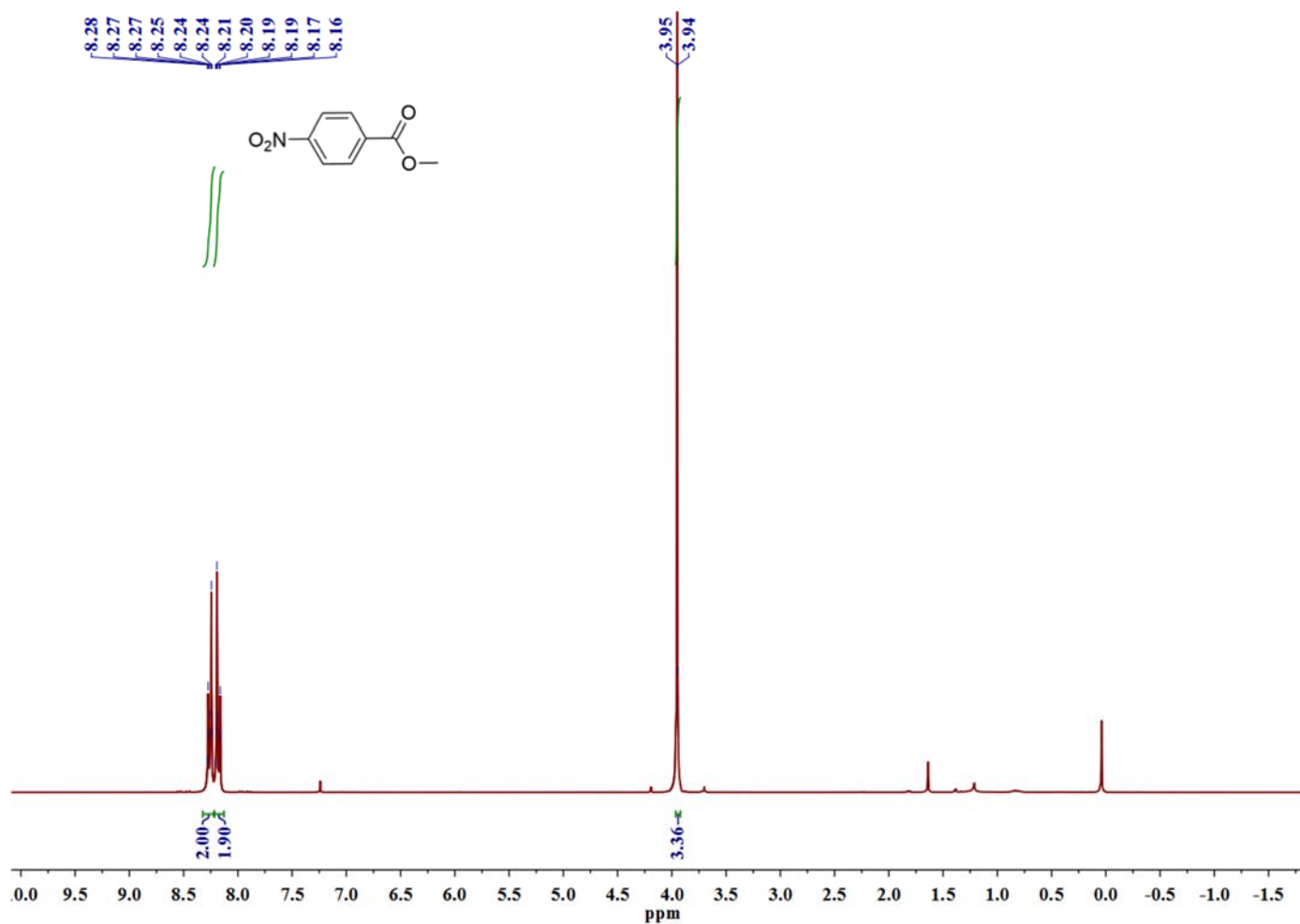


**Figure S10.**  $^1\text{H}$  NMR of methyl benzoate.

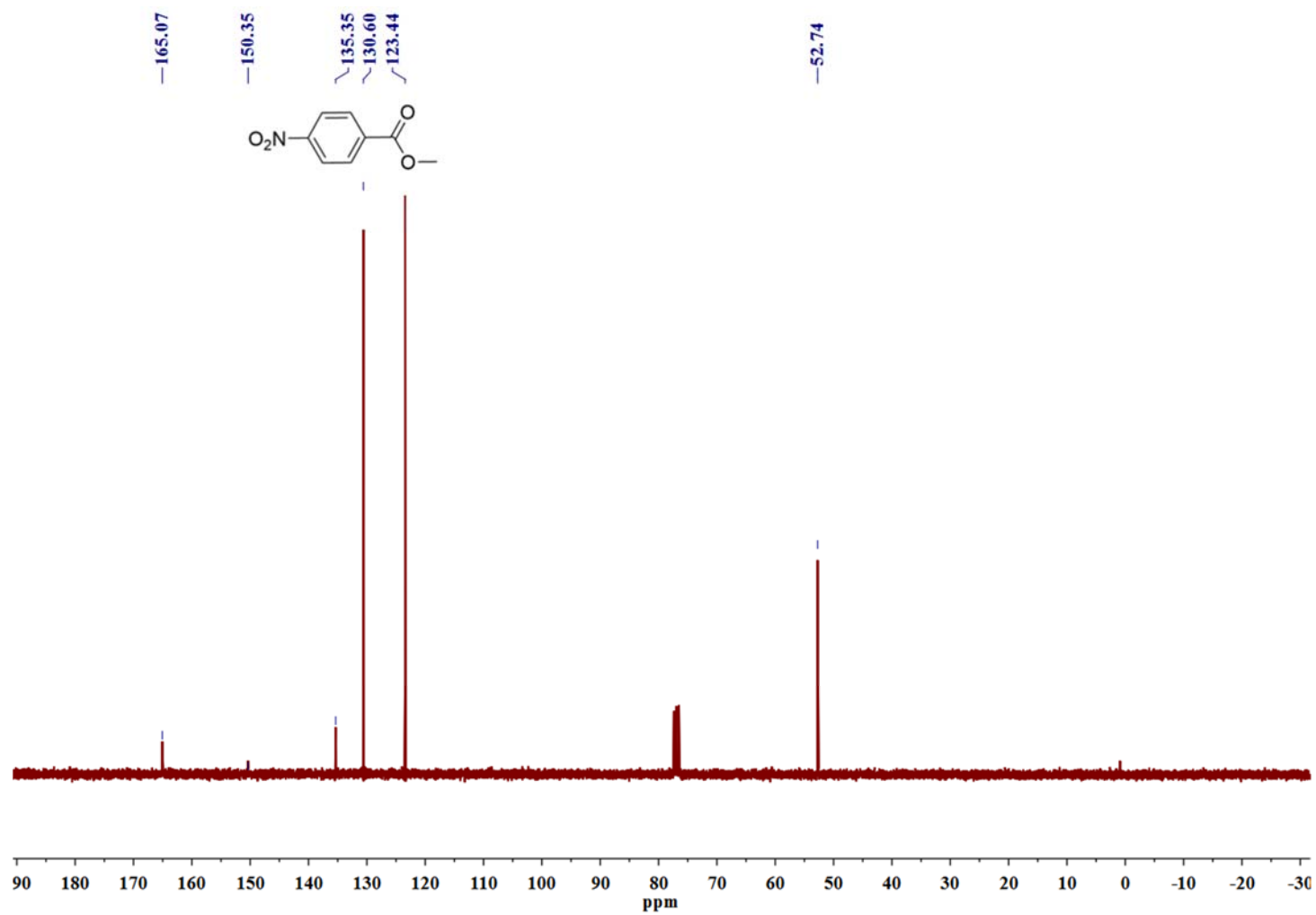


**Figure S11.**  $^{13}\text{C}$  NMR of methyl benzoate.

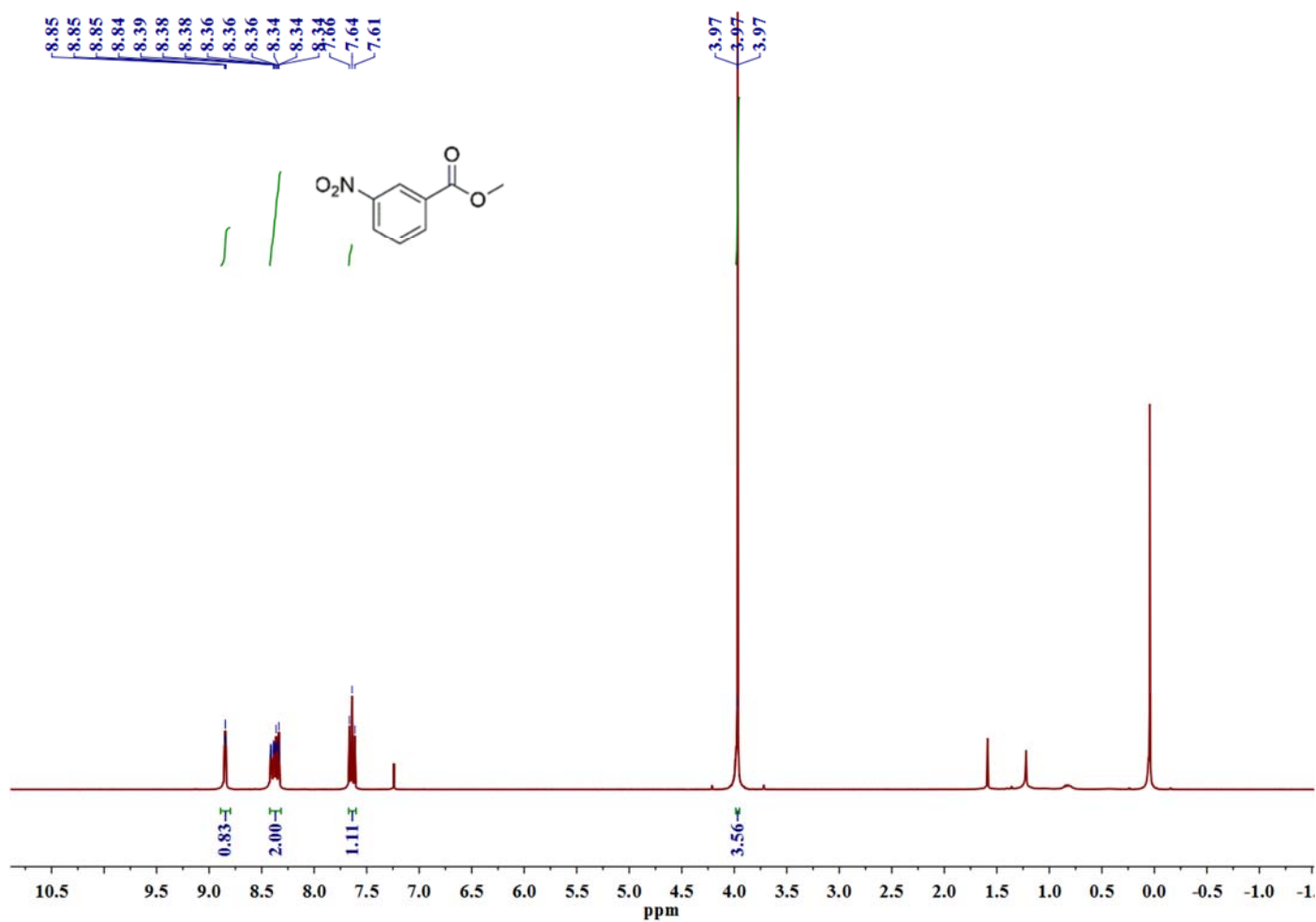




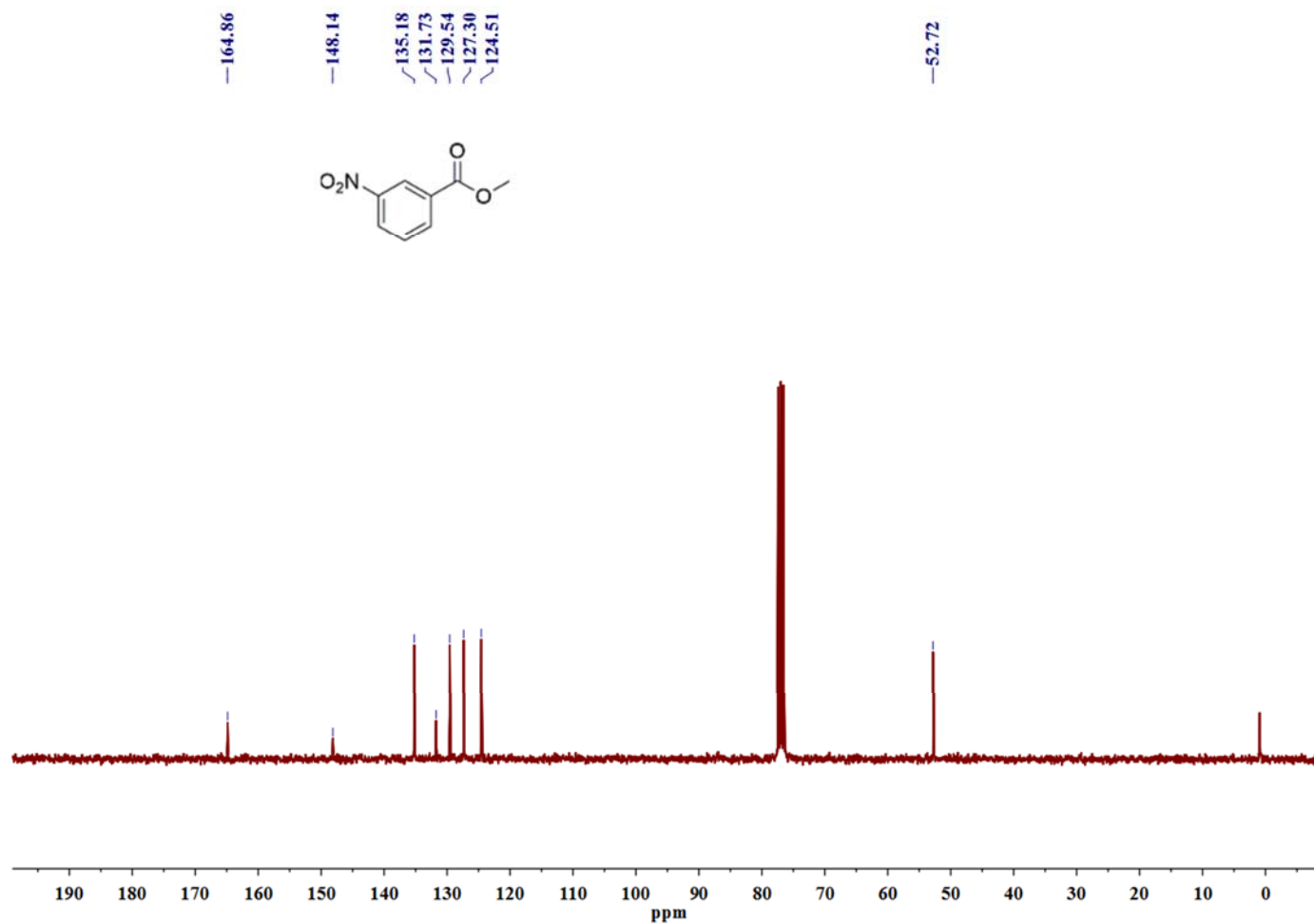
**Figure S12.** <sup>1</sup>H NMR of methyl 4-nitrobenzoate.



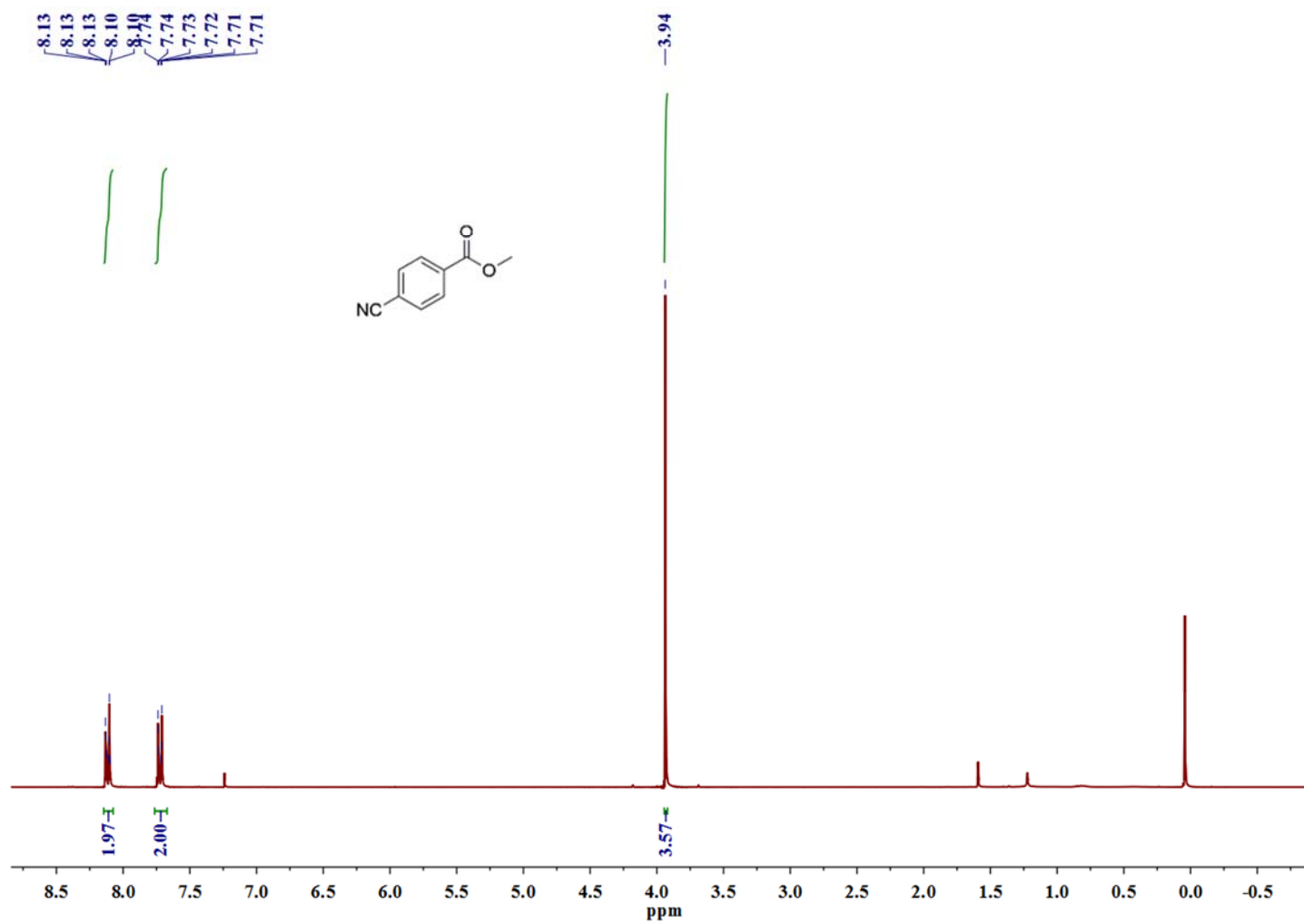
**Figure S13.**  $^{13}\text{C}$  NMR of methyl 4-nitrobenzoate.



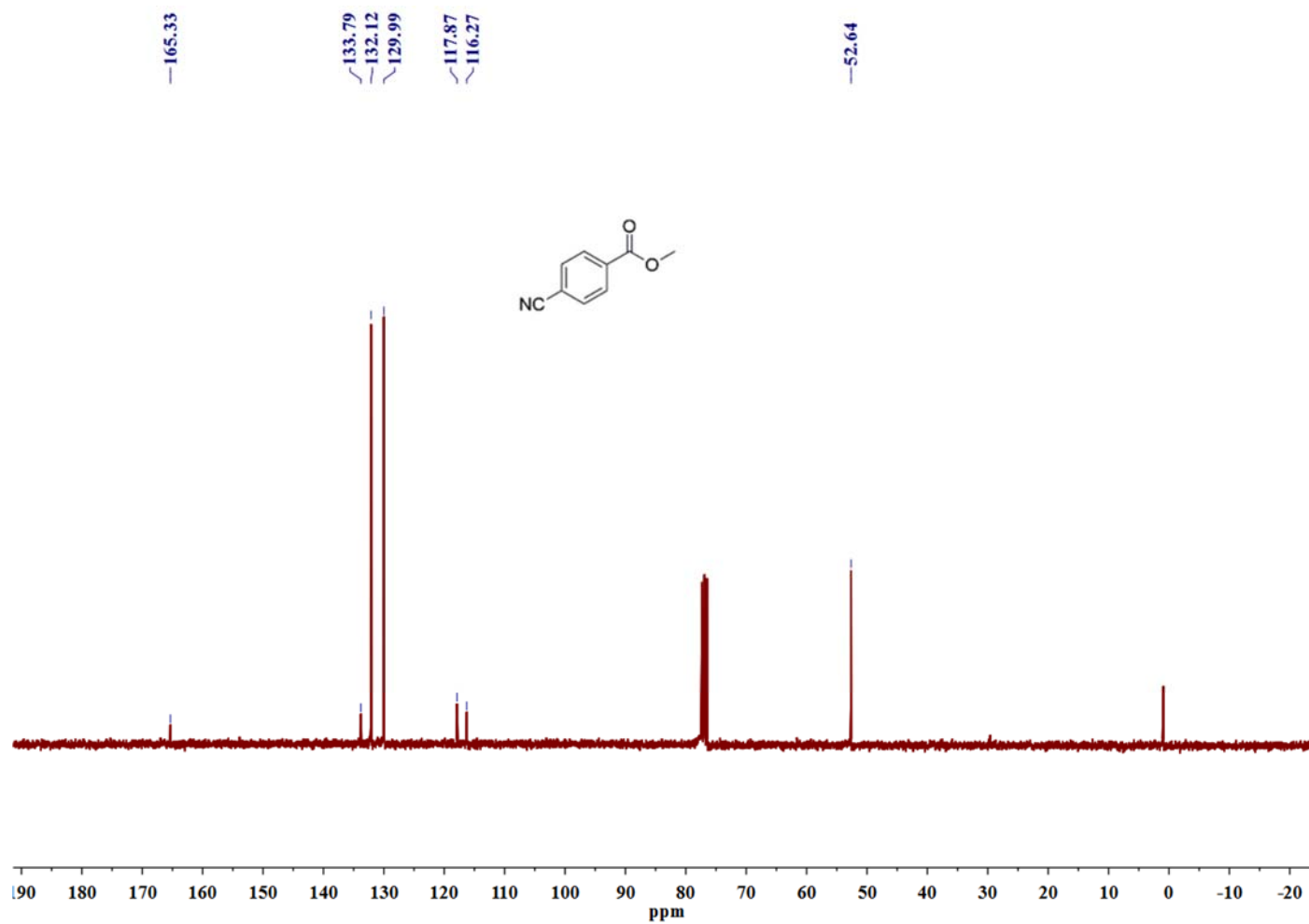
**Figure S14.**  $^1\text{H}$  NMR of methyl 3-nitrobenzoate.



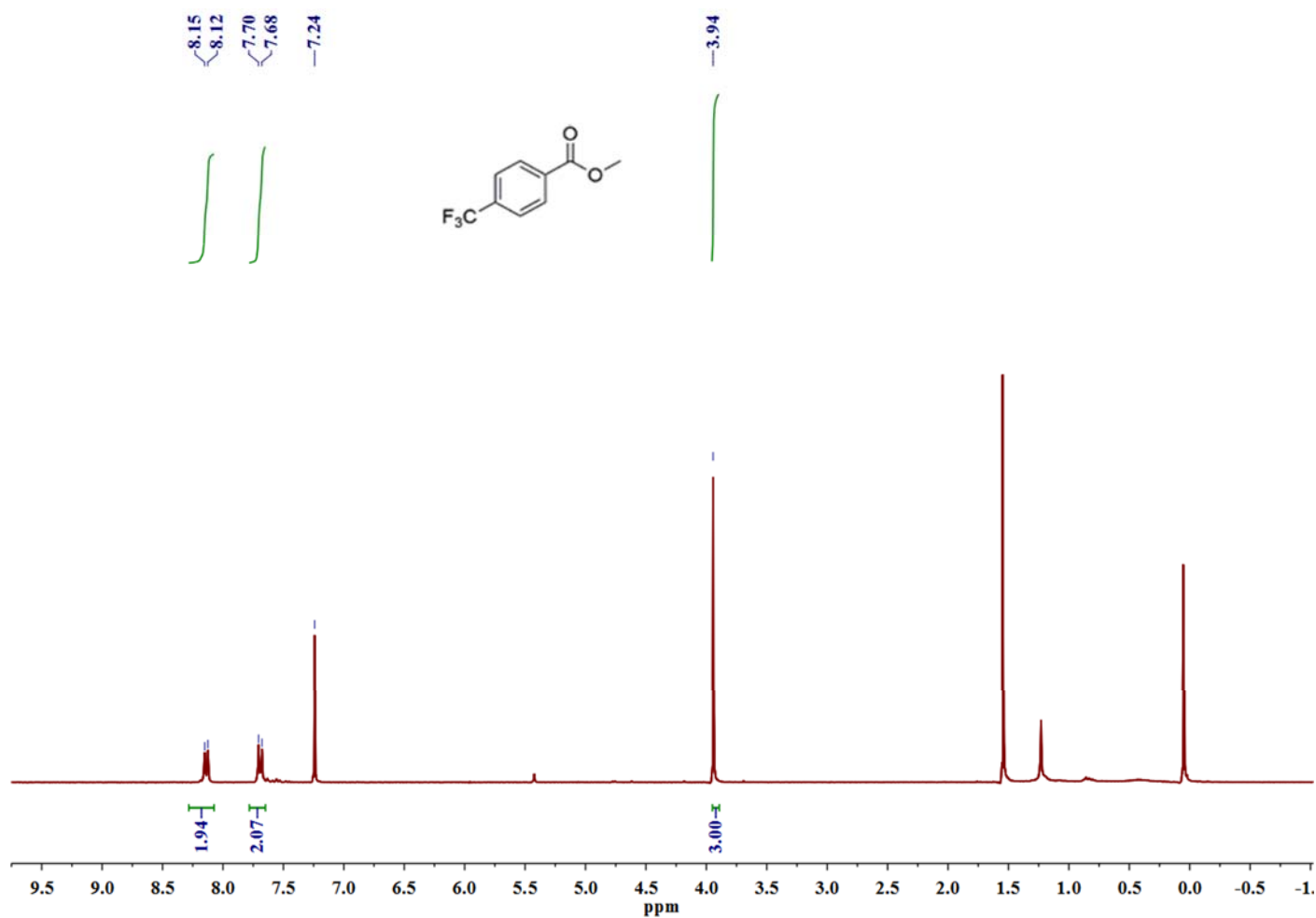
**Figure S15.** <sup>13</sup>C NMR of methyl 3-nitrobenzoate.



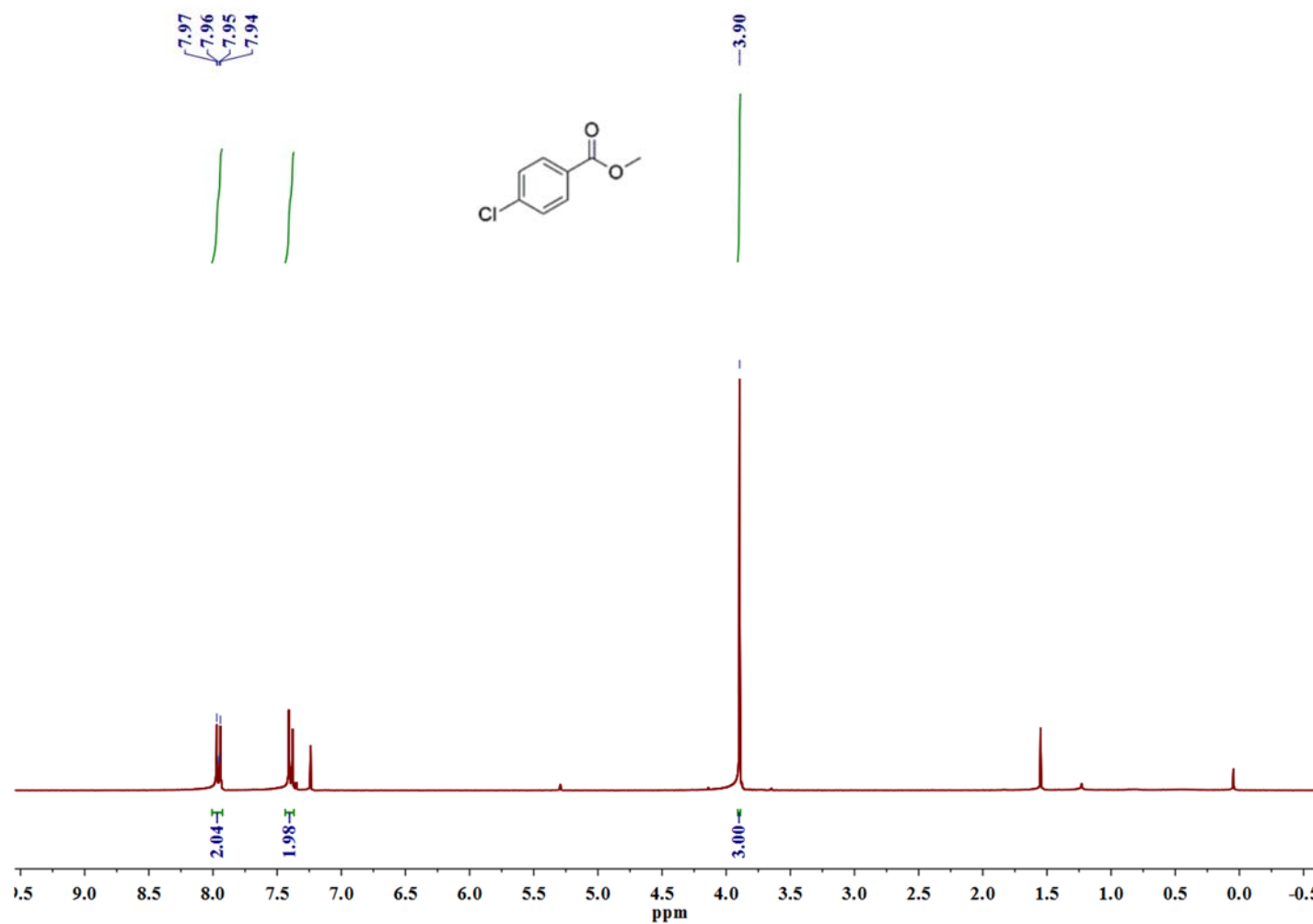
**Figure S16.**  $^1\text{H}$  NMR of methyl 4-cyanobenzoate.



**Figure S17.**  $^{13}\text{C}$  NMR of methyl 4-cyanobenzoate.

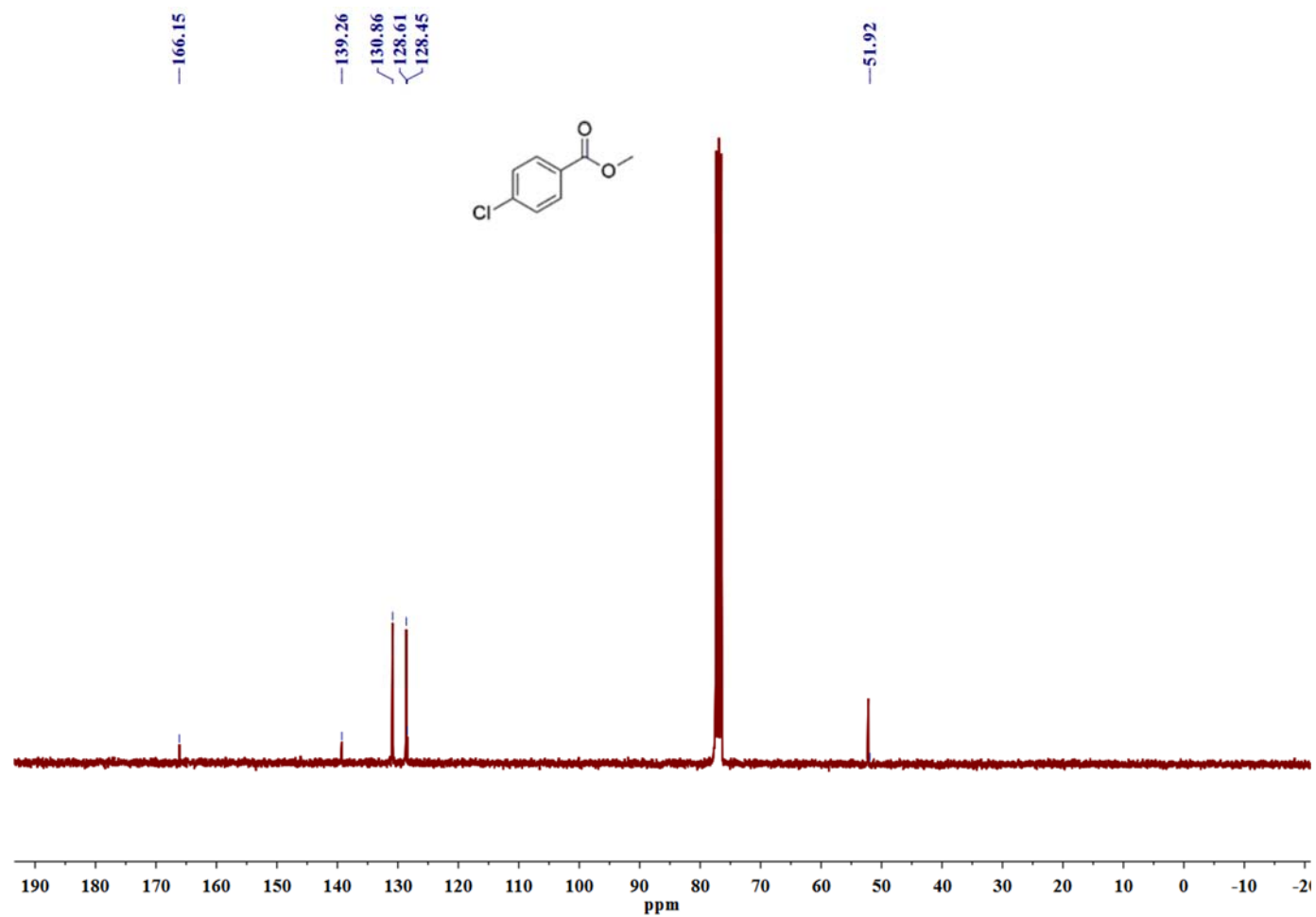


**Figure S18.**  $^1\text{H}$  NMR of methyl 4-trifluoromethylbenzoate.

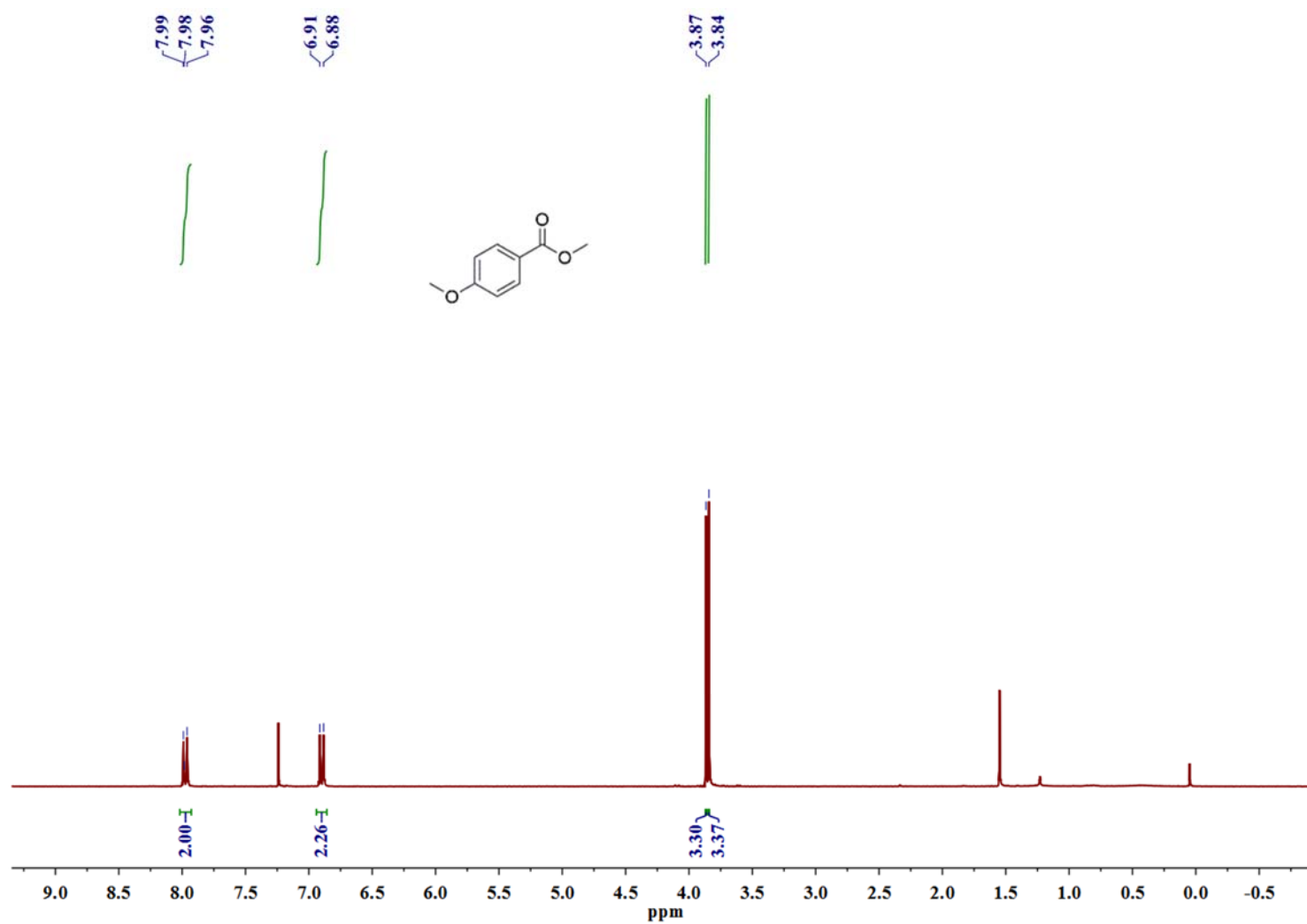


**Figure S19.** <sup>1</sup>H NMR of methyl 4-chlorobenzoate.

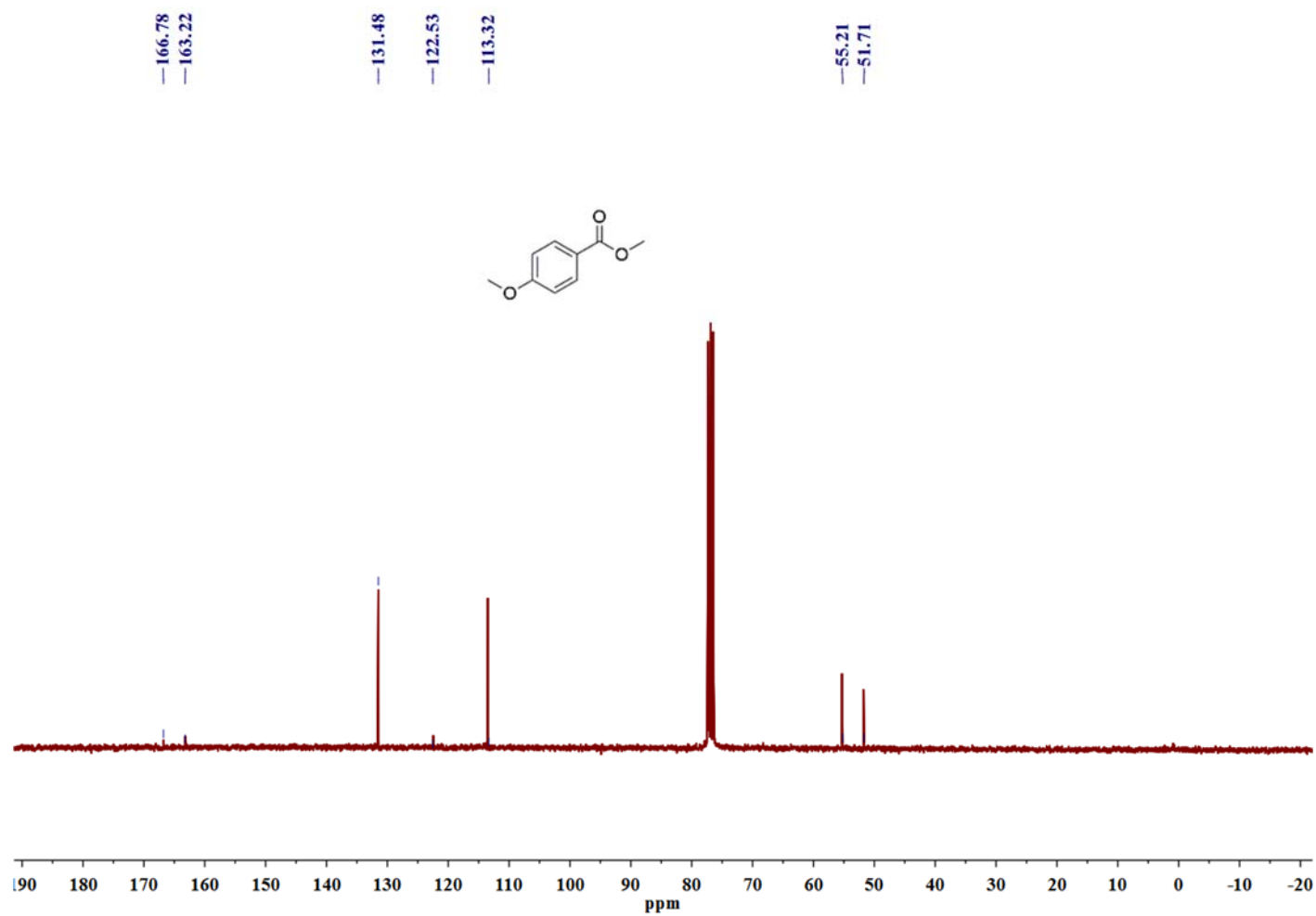




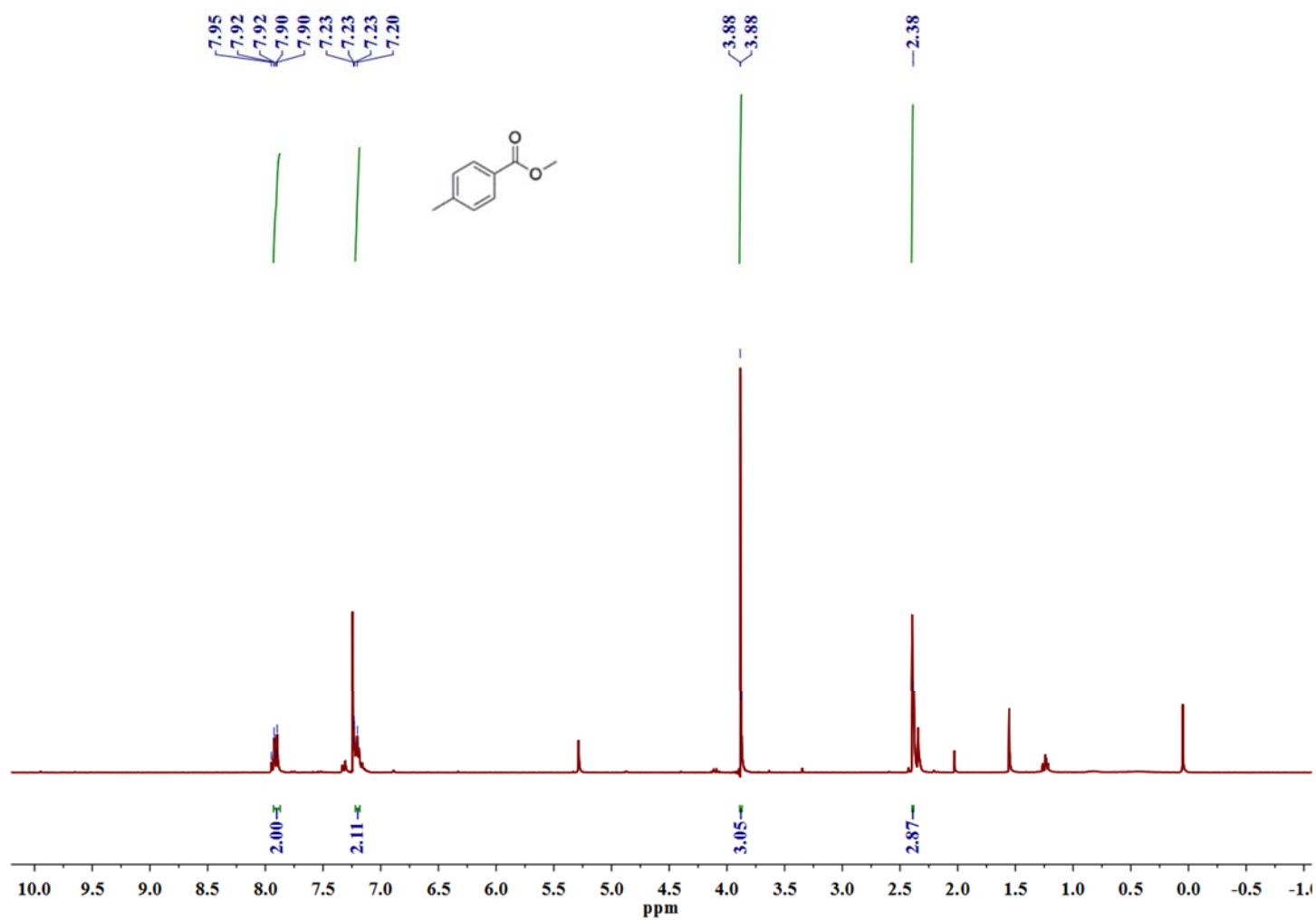
**Figure S20.**  $^{13}\text{C}$  NMR of methyl 4-chlorobenzoate.



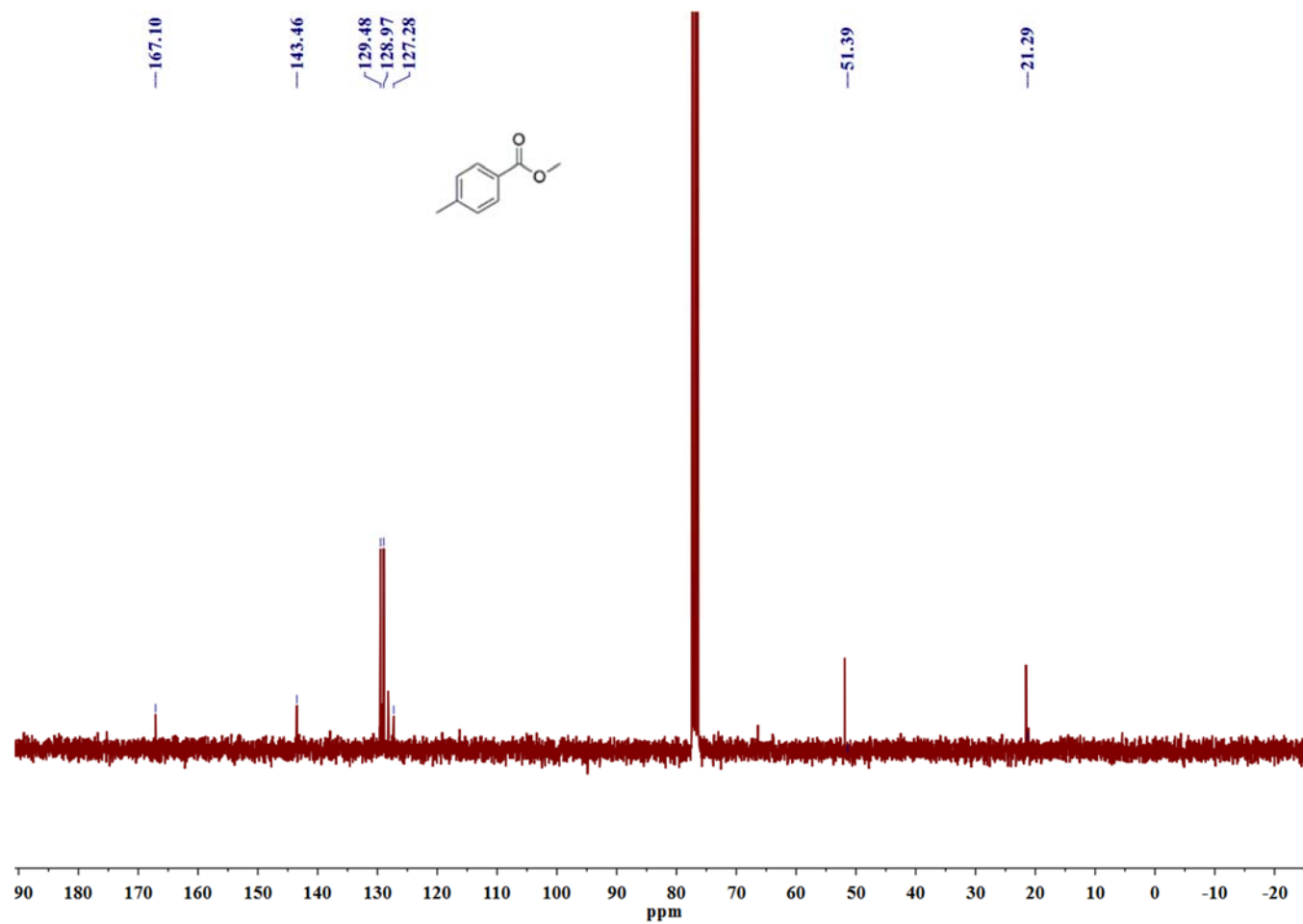
**Figure S21.**  $^1\text{H}$  NMR of methyl 4-methoxybenzoate.



**Figure S22.**  $^{13}\text{C}$  NMR of methyl 4-methoxybenzoate.



**Figure S23.** <sup>1</sup>H NMR of methyl 4-methylbenzoate.



**Figure S24.**  $^{13}\text{C}$  NMR of methyl 4-methylbenzoate.

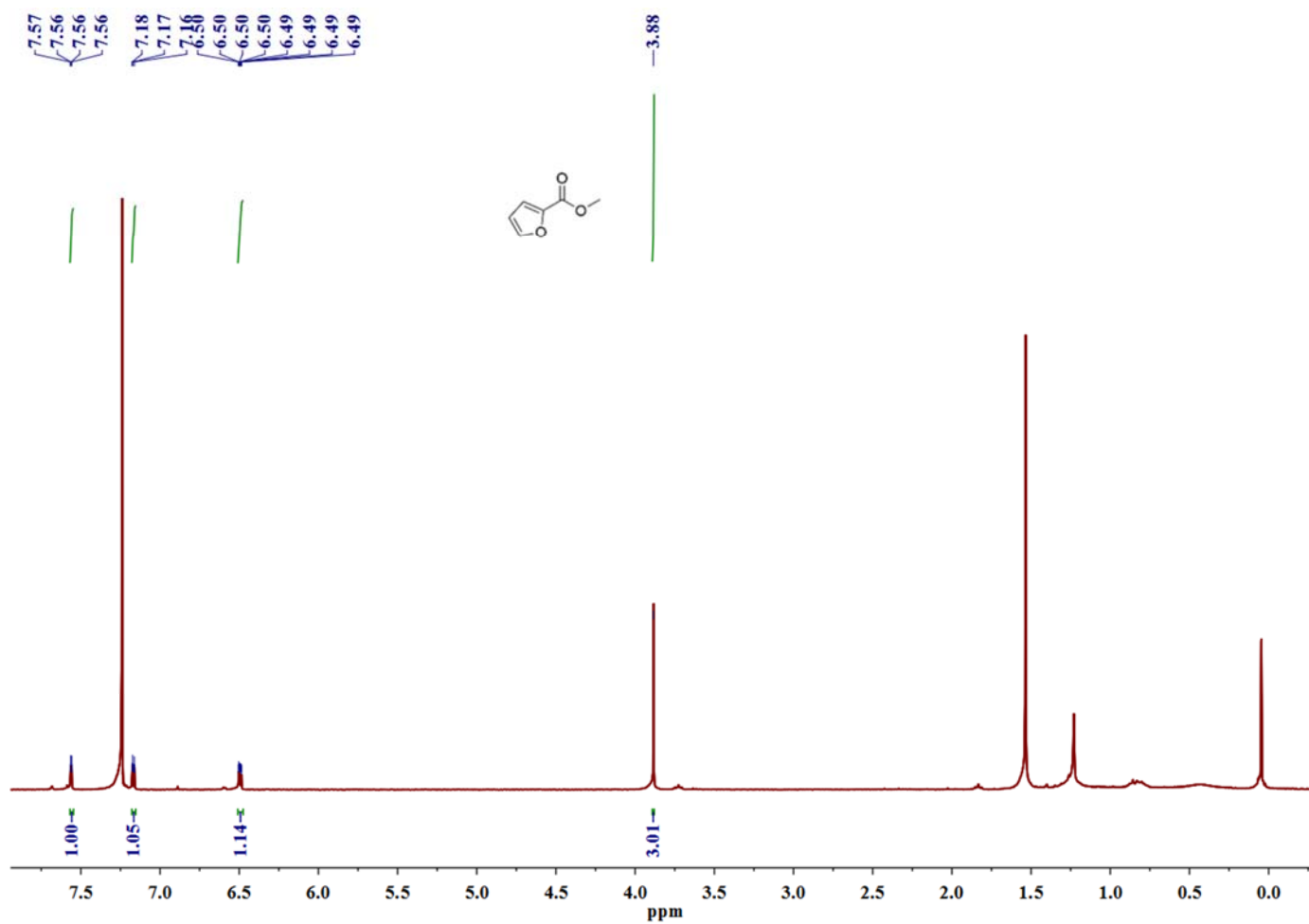
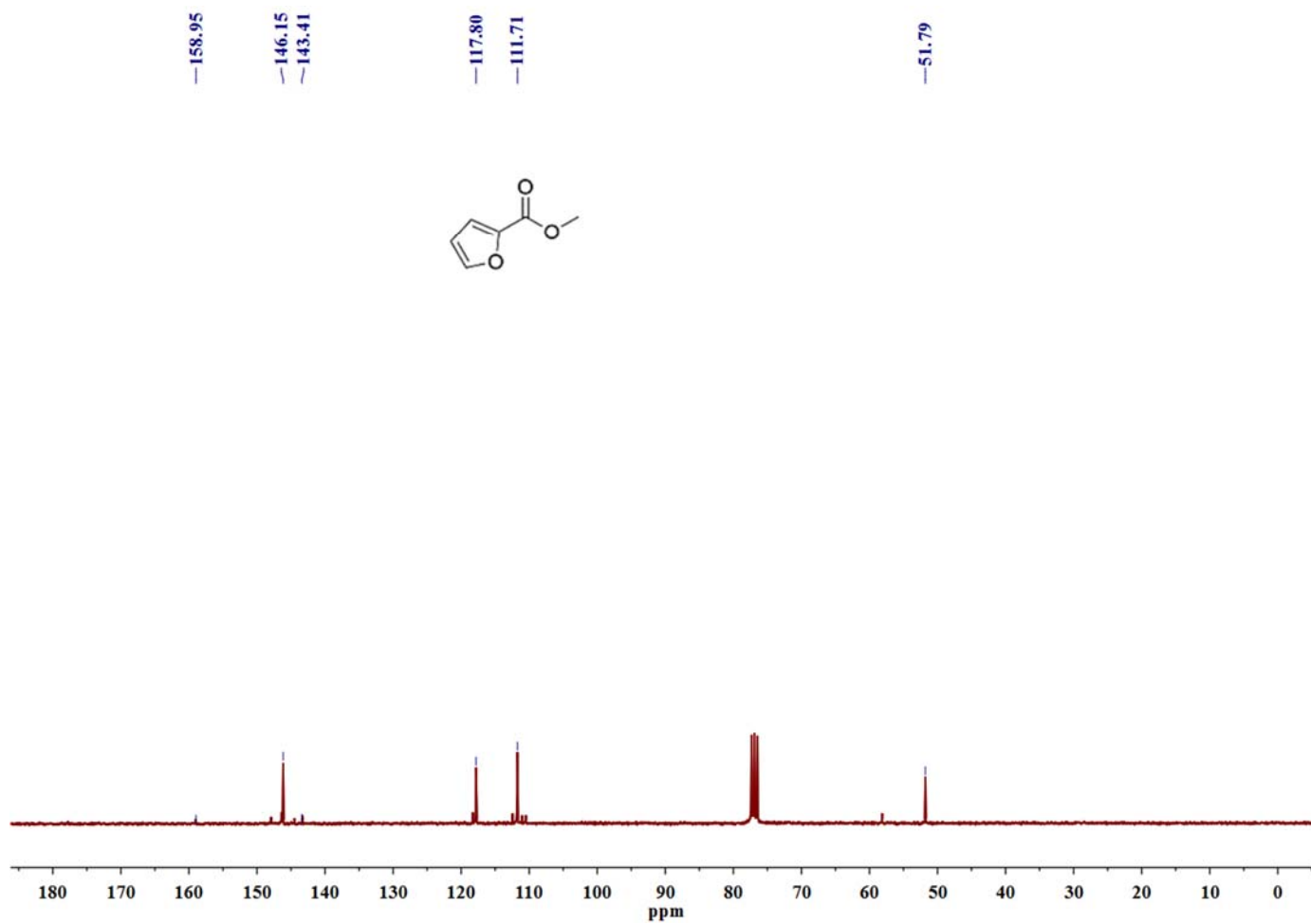


Figure S25. <sup>1</sup>H NMR of methyl 2-furoate.



**Figure S26.**  $^{13}\text{C}$  NMR of methyl 2-furoate.

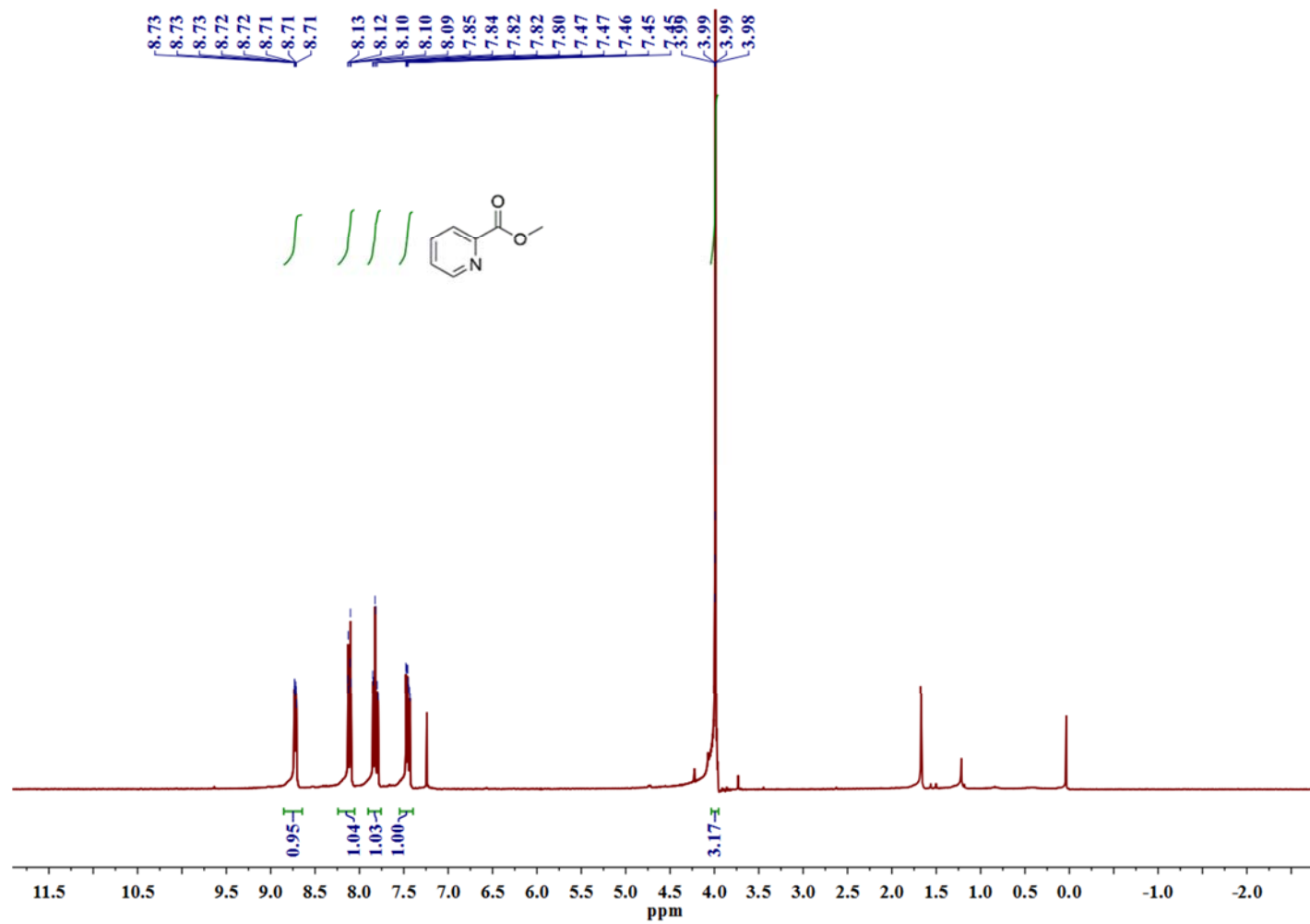
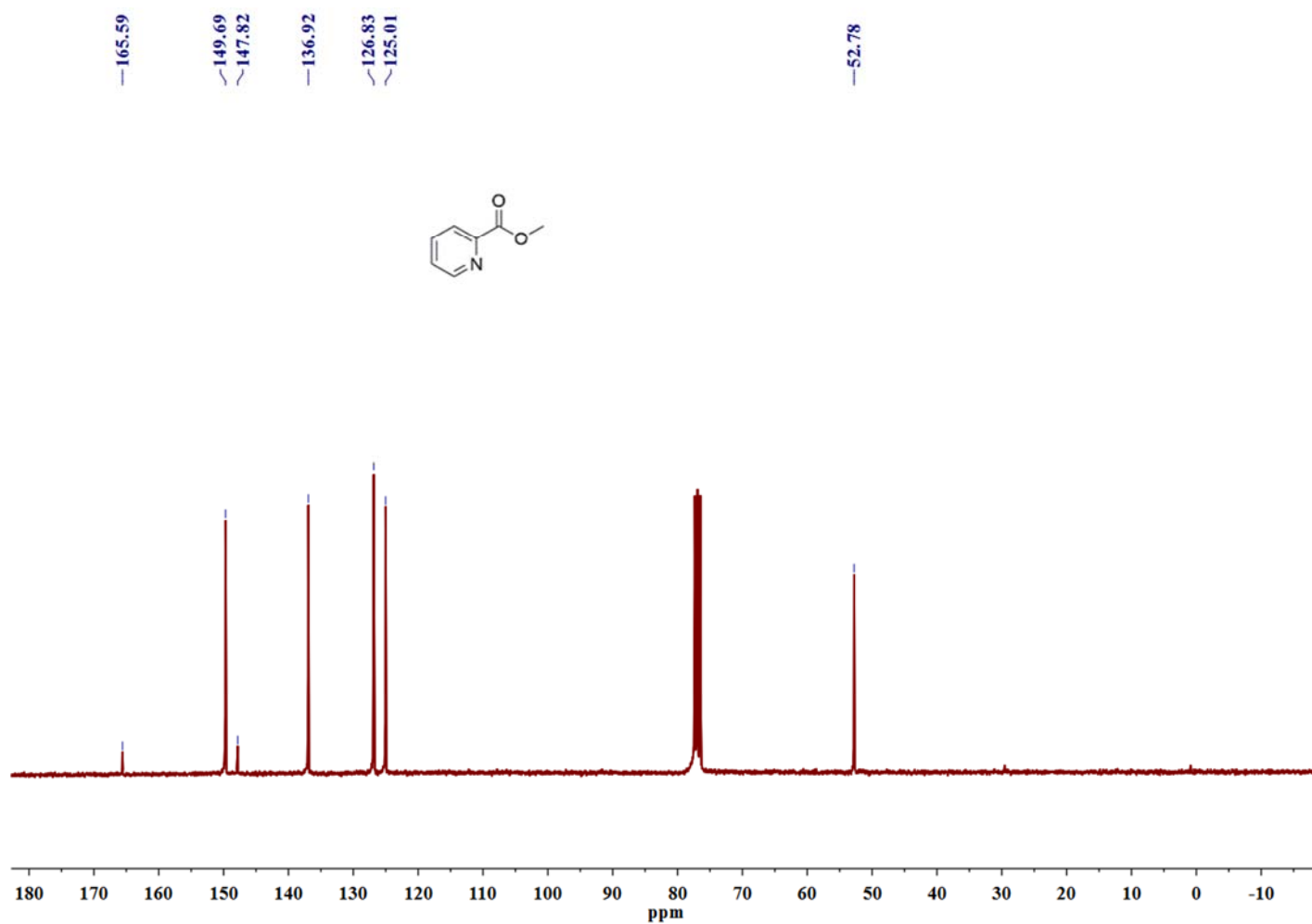


Figure S27.  $^1\text{H}$  NMR of methyl 2-picolinate.





**Figure S28.** <sup>13</sup>C NMR of methyl 2-picolinate.

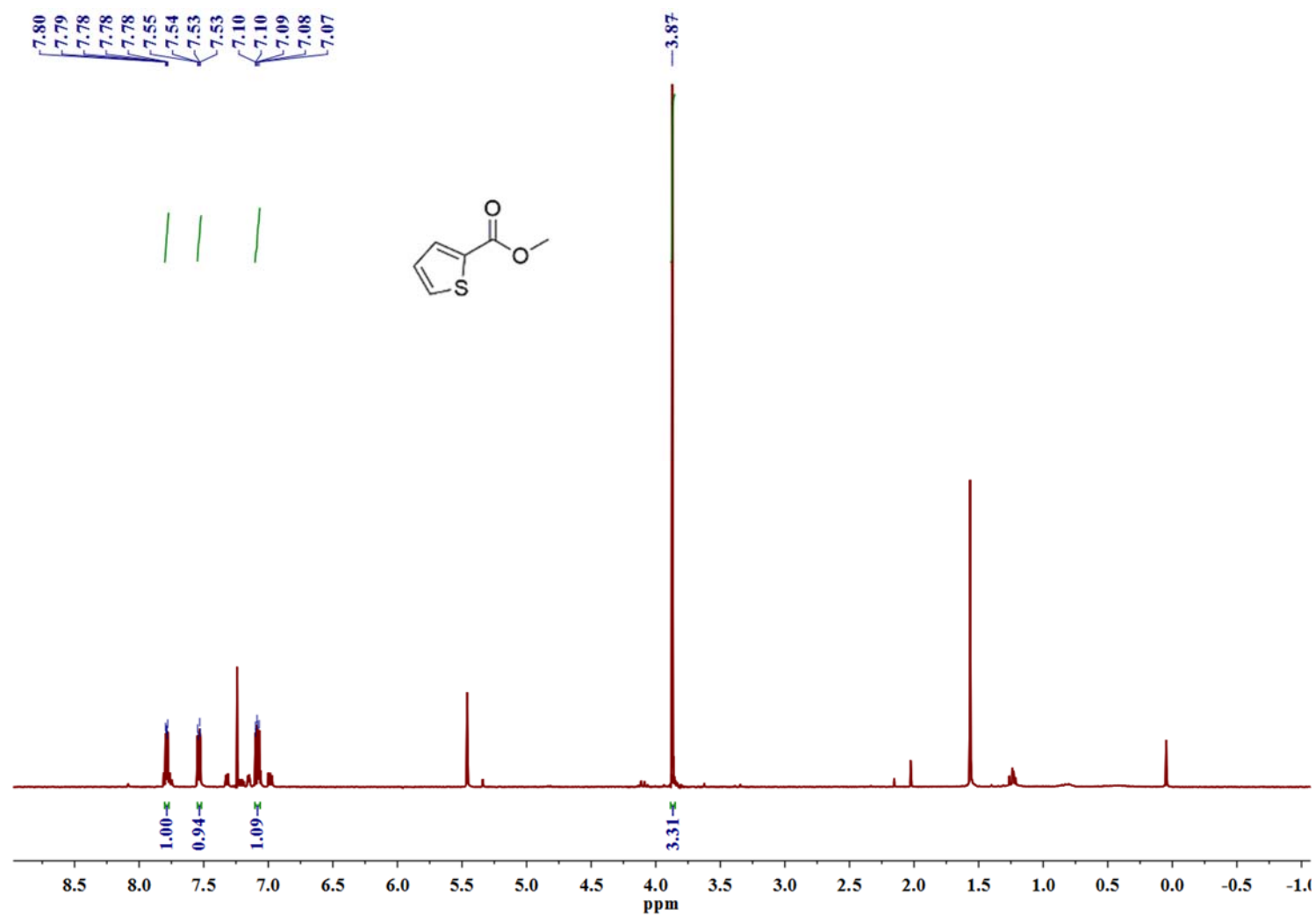
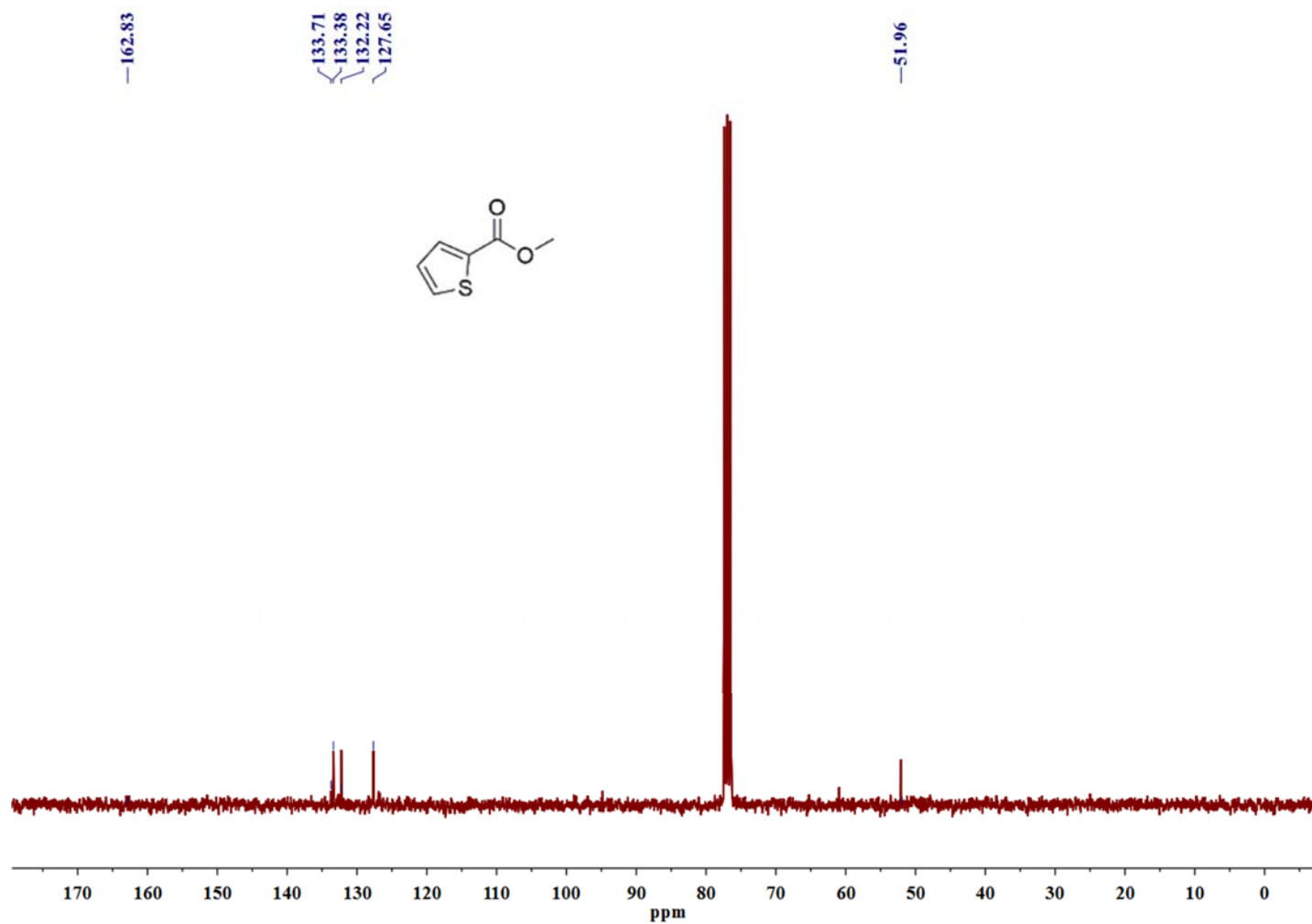
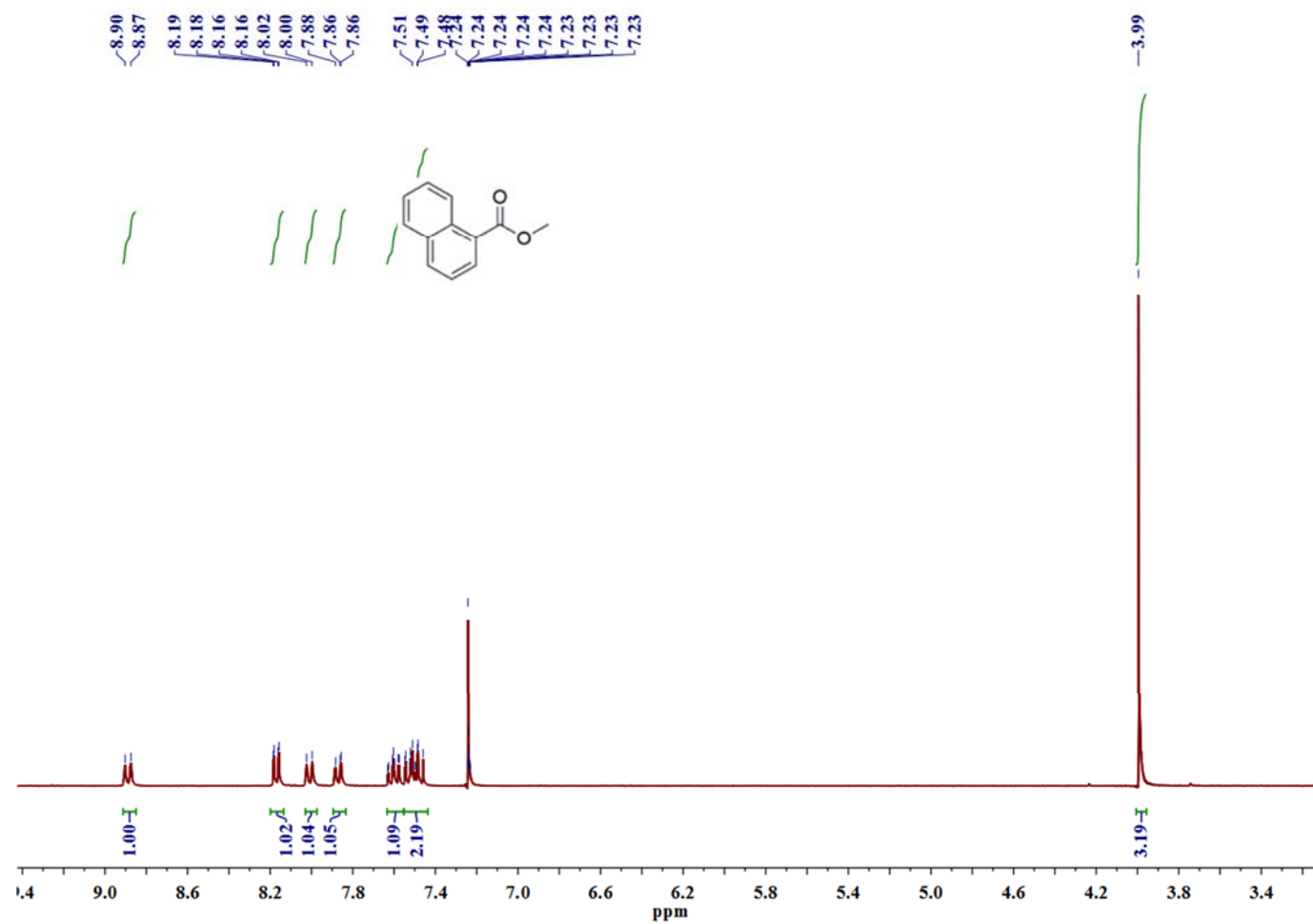


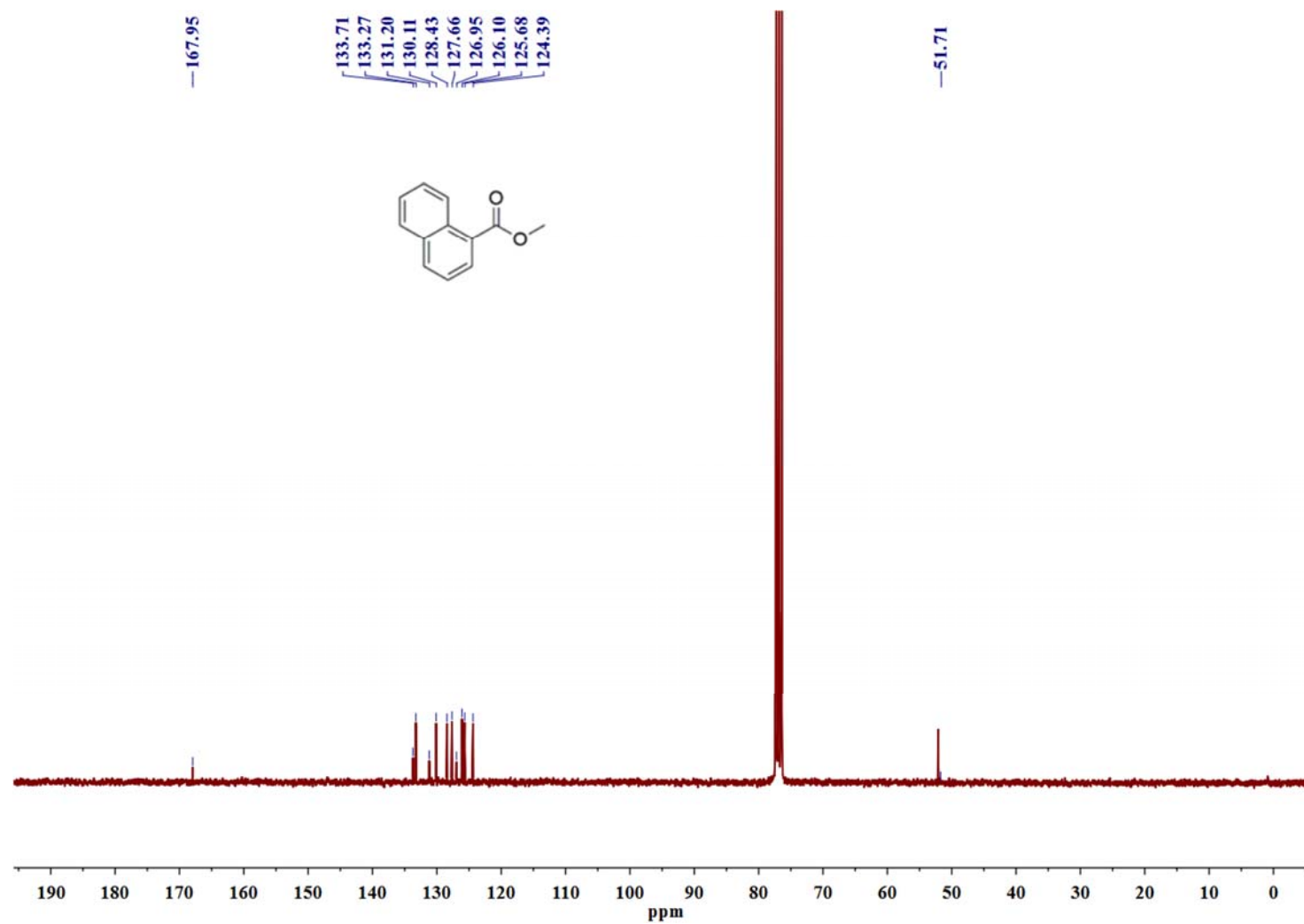
Figure S29.  $^1\text{H}$  NMR of methyl 2-thenoate.



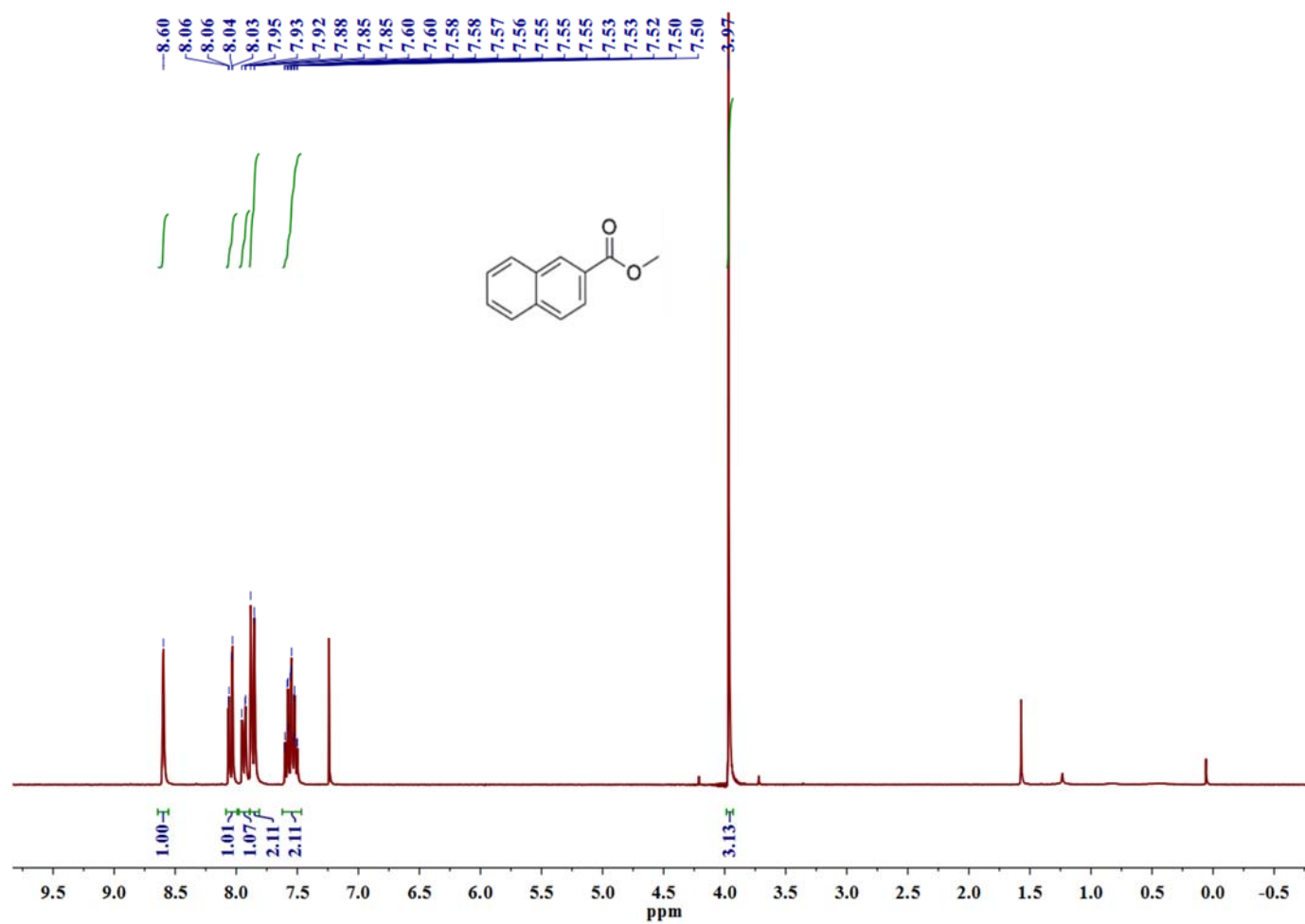
**Figure S30.**  $^{13}\text{C}$  NMR of methyl 2-thenoate.



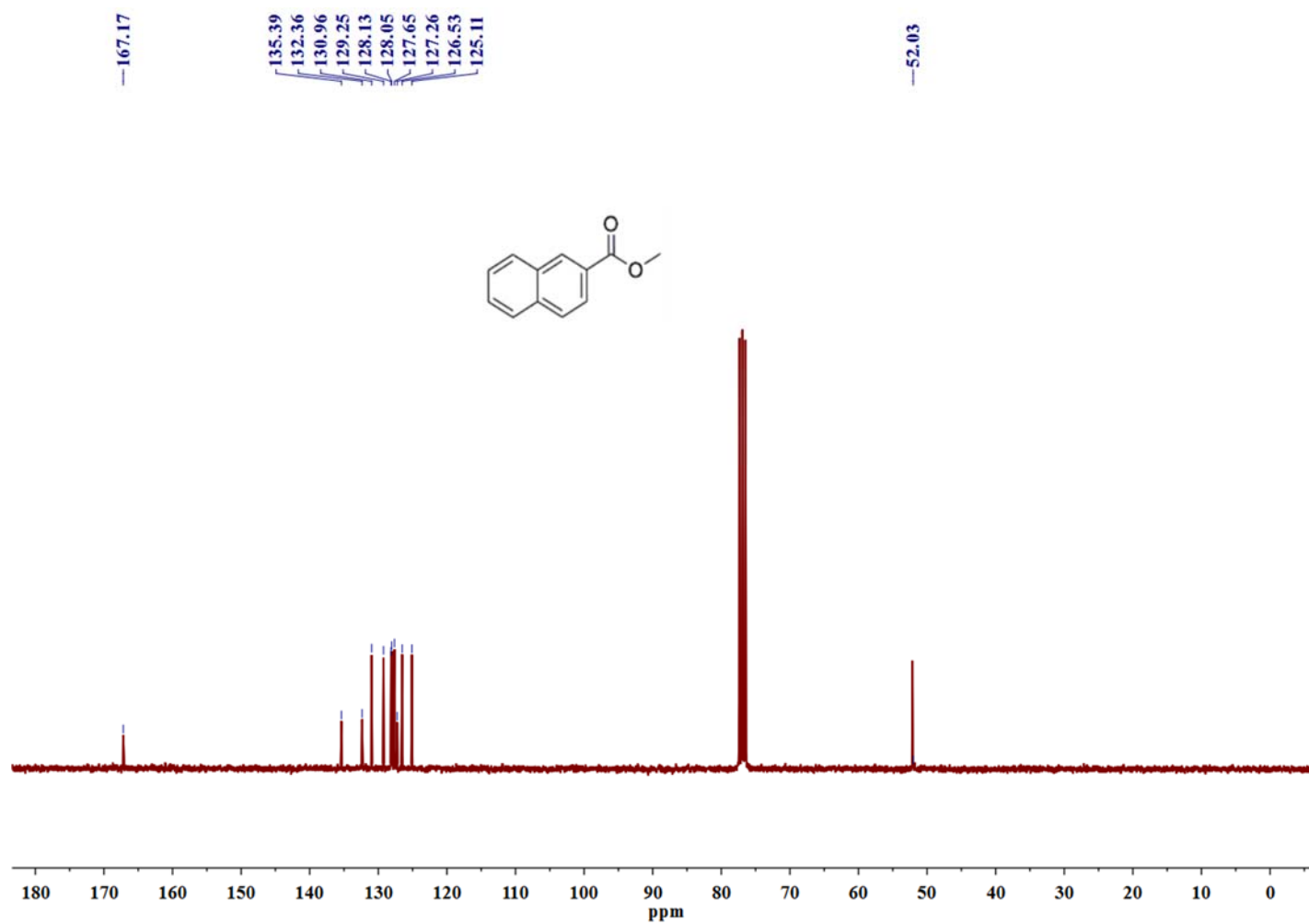
**Figure S31.** <sup>1</sup>H NMR of methyl naphthalene-1-carboxylate.



**Figure S32.**  $^{13}\text{C}$  NMR of methyl naphthalene-1-carboxylate.



**Figure S33.** <sup>1</sup>H NMR of methyl naphthalene-2-carboxylate.



**Figure S34.** <sup>13</sup>C NMR of methyl naphthalene-2-carboxylate.

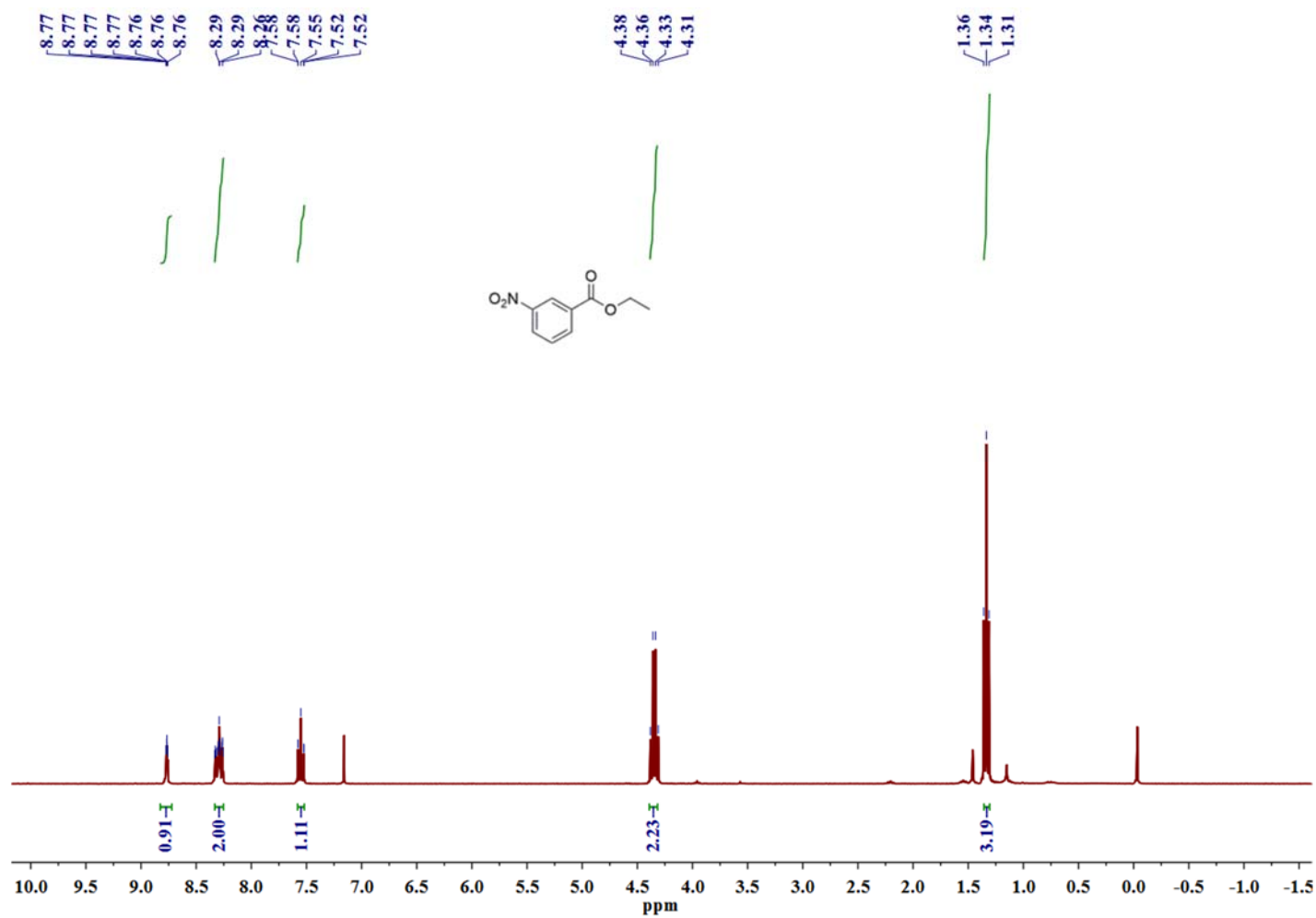


Figure S35. <sup>1</sup>H NMR of ethyl 3-nitrobenzoate.



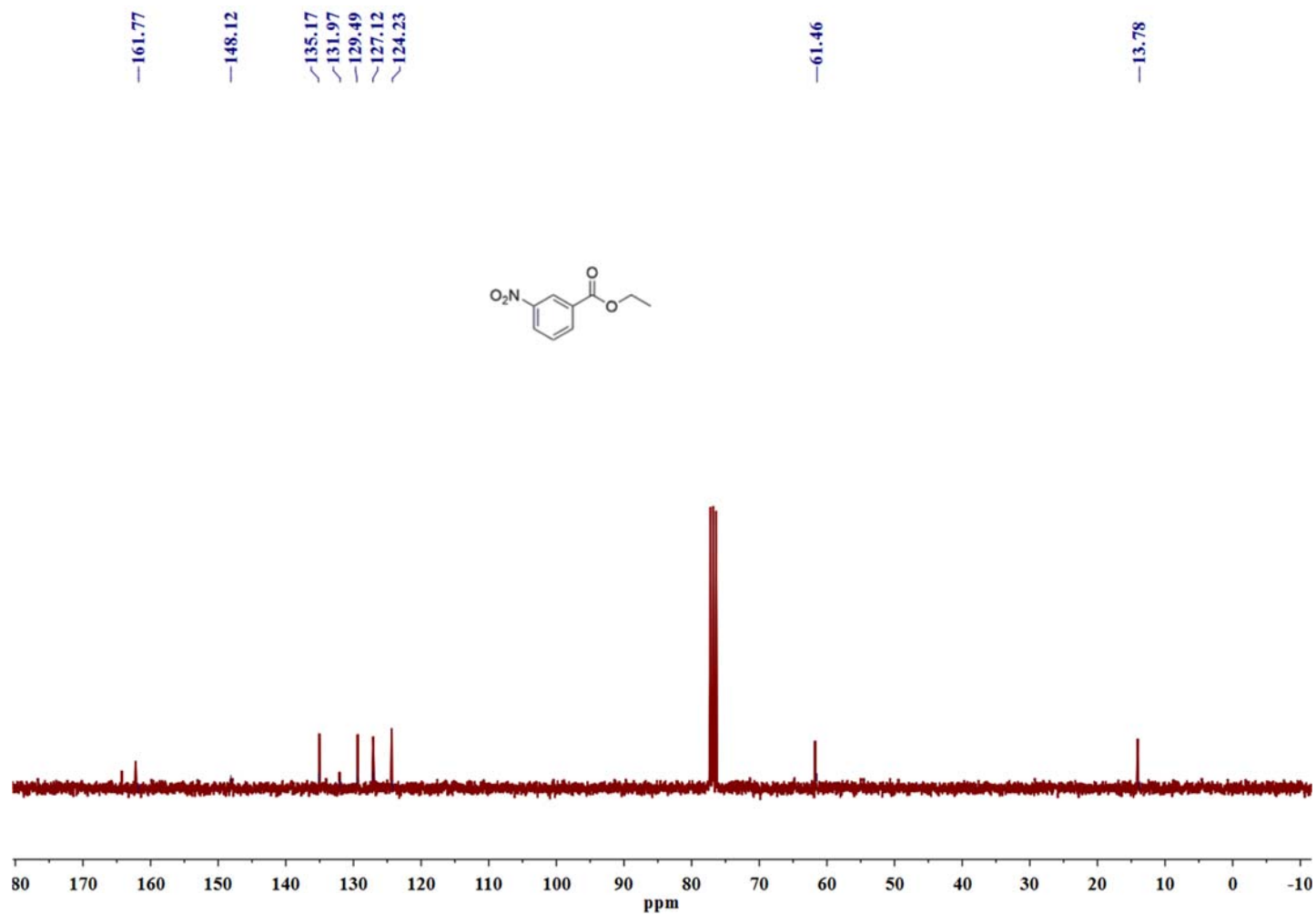


Figure S36. <sup>13</sup>C NMR of ethyl 3-nitrobenzoate.

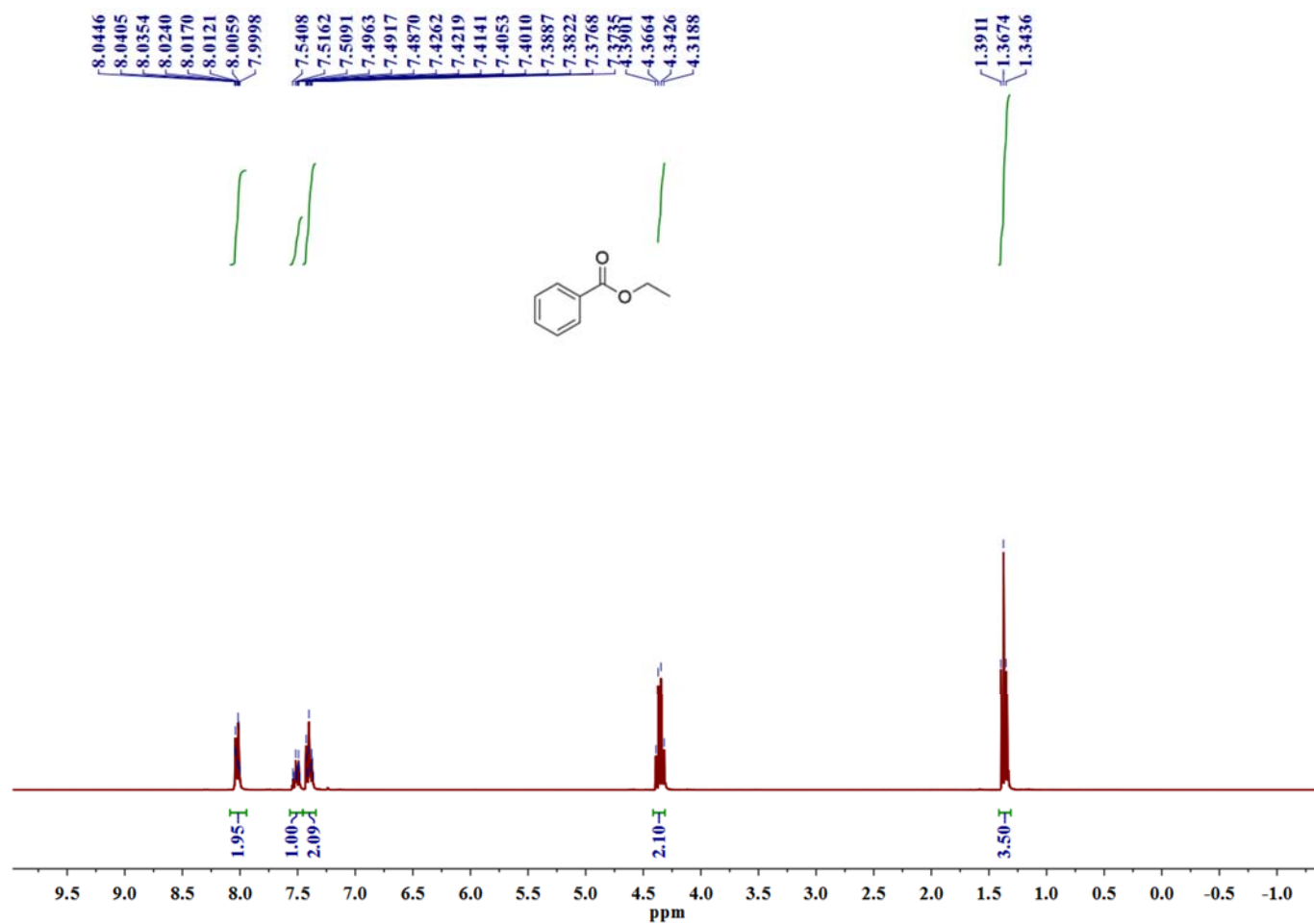
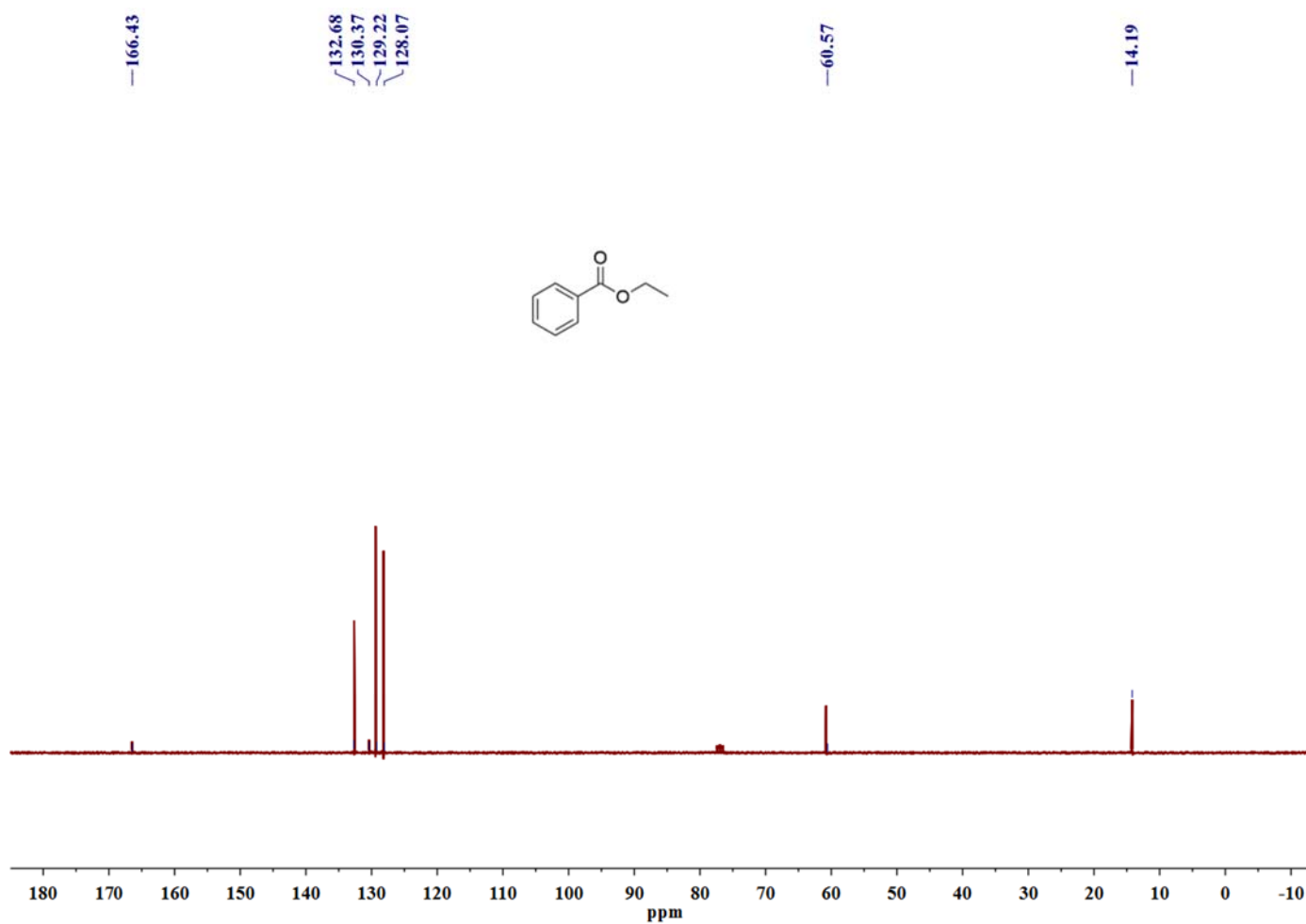
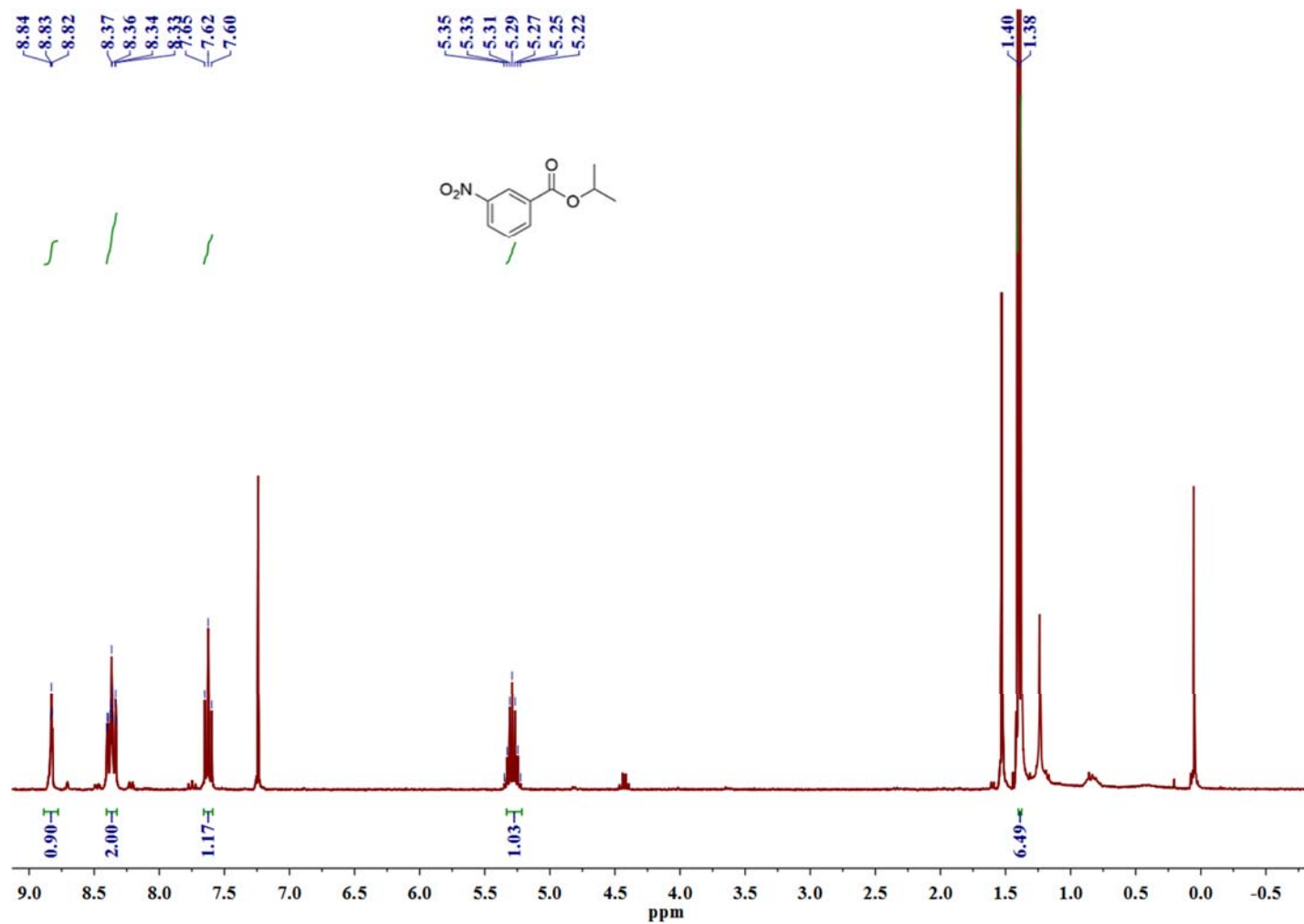


Figure S37.  $^1\text{H}$  NMR of ethyl benzoate.



**Figure S38.**  $^{13}\text{C}$  NMR of ethyl benzoate.



**Figure S39.** <sup>1</sup>H NMR of isopropyl 3-nitrobenzoate.