

## Supporting Information

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### 1. General Information

All substrates and reagents were procured from commercial suppliers (Alfa-Aesar, Sigma-Aldrich, Merck, SD fine chemicals, HI Media) and were utilized without prior purification unless otherwise indicated. All reactions were conducted in a 10 mL round bottom flask with magnetic stirring. Solvents employed in purification and extraction were distilled prior to use. Thin-layer chromatography (TLC) was carried-out on TLC plates availed from Merck. Compounds were observed by immersion in KMnO<sub>4</sub> staining solution followed by heating or with UV light ( $\lambda = 254$  nm). Products were purified by CombiFlash MPLC. All HRMS spectra are recorded using 6545 QTOF LC/MS, Agilent instrument equipped with an auto sampler in EI-QTOF method in acetonitrile solvent. <sup>1</sup>H (<sup>13</sup>C) NMR spectra were recorded at 400 (100) MHz on a Bruker spectrometer using CDCl<sub>3</sub> and DMSO-*d*<sub>6</sub> as a solvent. The <sup>1</sup>H and <sup>13</sup>C chemical shifts were referenced to residual solvent signals at  $\delta_{\text{H/C}}$  7.26/77.28 (CDCl<sub>3</sub>) and  $\delta_{\text{H/C}}$  2.51/39.50 (DMSO-*d*<sub>6</sub>) relative to TMS as internal standards. Coupling constants *J* [Hz] were directly taken from the spectra and are not averaged. Splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), overlapped and br (broad).

**2. Synthesis of Hematite iron oxide ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) nano-particles:** Hematite iron oxide ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) nano-particles are obtained from starting Fe(NO<sub>3</sub>)<sub>3</sub> (2.0 g, 8.3 mmol) using auto-combustion method. The Fe(NO<sub>3</sub>)<sub>3</sub> is mixed in distilled H<sub>2</sub>O (100 mL), then 3 equivalents of glycine (1.86 g, 24.5 mmol) was added in the solution and heated at 100 °C for 1 hour. The amino acid glycine assist during chelation and combustion process. The temperature of the reaction mass is the excelled up to 150 °C to induce the auto-combustion process. The glycine and NO<sub>3</sub><sup>-</sup> ion act as reducing and oxidizing agents, and these assist in thermally induced redox reaction. These auto-combustion process lead to the release of excessive amounts of heat that transform the Fe(III)-glycine complex into dried Fe<sub>2</sub>O<sub>3</sub> particles, which

is then calcined at 600 °C for 2 hours to achieve 1.0 g of the crystalline hematite Fe<sub>2</sub>O<sub>3</sub> particles with 80% yield.

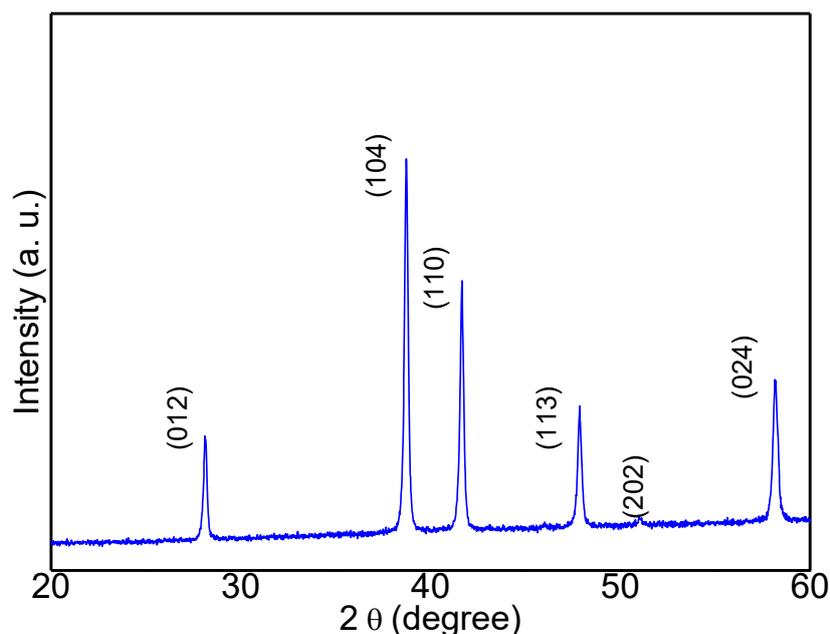
### 3. General Experimental Procedure for the Synthesis of Products **3aa-ai** and **3ba, bg, ca, cg, ch, dg** using HMPT

A 10 mL round bottom flask was charged with enones **1a-d** (1.0 mmol), azoles **2a-i** (1.0 mmol) in MeCN (2 mL), then added P(NMe<sub>2</sub>)<sub>3</sub> (1.1 mmol) and the reaction mixture was stirred at room temperature (25 °C) for 1-5 hours. After completion of the reaction (progress was monitored by TLC; SiO<sub>2</sub>, Hexane/EtOAc = 8:2 and LC-MS), the reaction mixture was quenched with saturated NaHCO<sub>3</sub> solution, diluted with water (20 mL) and extracted with ethyl acetate (3 × 15 mL). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Solvent was removed under reduced pressure and the remaining residue was purified over CombiFlash MPLC using Hexane/EtOAc = 80:20 as an eluent to obtain the desired Aza-Michael addition products **3aa-ai** and **3ba, bg, ca, cg, ch, dg** in high yields.

### 4. General Experimental Procedure for the Synthesis of Products **3aa-ai** and **3ba, bg, ca, cg, ch, dg** using Fe<sub>2</sub>O<sub>3</sub> nanoparticles as Recyclable Catalyst

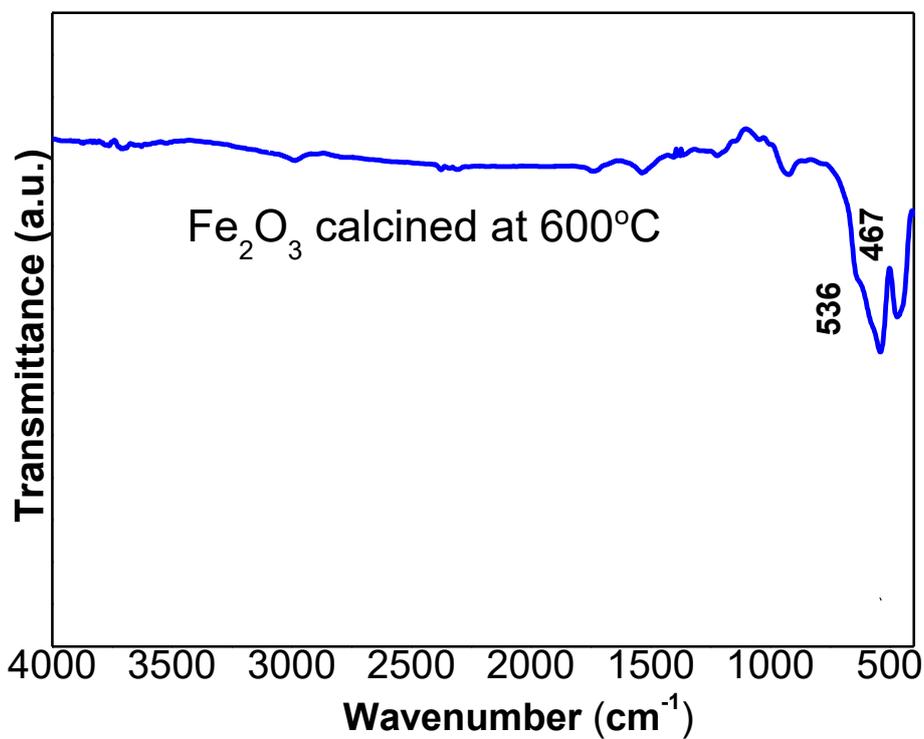
A 10 mL round bottom flask was charged with enones **1a-d** (1.0 mmol), azoles **2a-i** (1.0 mmol) in MeCN (2 mL), then Fe<sub>2</sub>O<sub>3</sub> nanoparticles (0.1 mmol) was added and the reaction mixture was stirred at 50 °C for 5 hours. After completion of the reaction (progress was monitored by TLC; SiO<sub>2</sub>, Hexane/EtOAc = 8:2 and LC-MS), the catalyst was isolated by the process of centrifugation. The reaction mixture was exposed towards the extraction process to obtain the crude product, which was purified by column chromatography. The isolated Fe<sub>2</sub>O<sub>3</sub>-NPs was cleansed with ethyl acetate, dried under vacuum and employed for next cycle of reaction without any reactivation or purification process.

### 5. Characterization data of Hematite iron oxide ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>)-nanoparticles



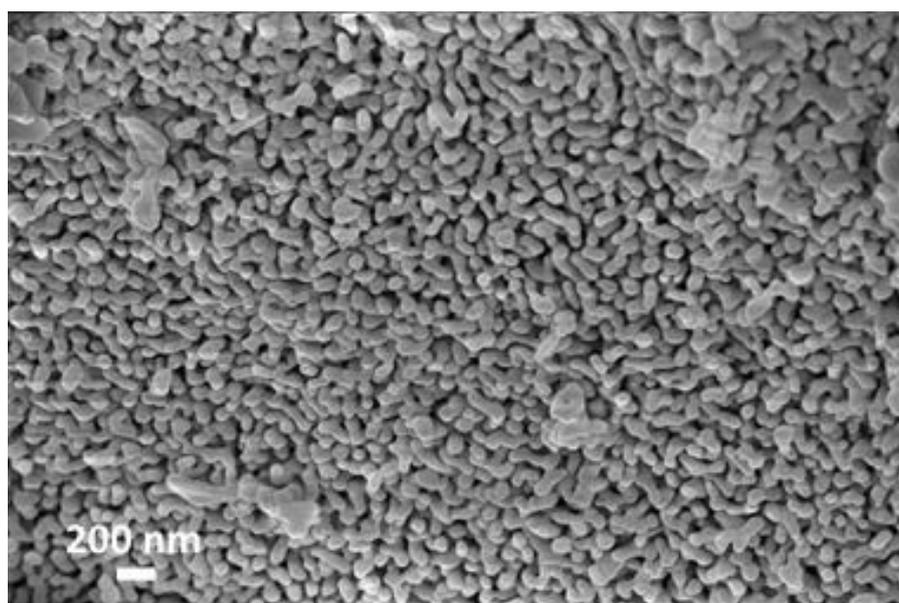
**Figure 1.** X-ray diffraction pattern of Fe<sub>2</sub>O<sub>3</sub>-nanoparticles calcined at 600 °C.

Figure 1 represents the X-ray diffraction (XRD) pattern (recorded under  $\text{CoK}\alpha$  radiation) of iron oxide ( $\text{Fe}_2\text{O}_3$ ) nanoparticles calcined at  $600^\circ\text{C}$  for 2 h. The XRD pattern is found to match well with the standard powder XRD pattern (JCPDS-card-33-0664) of hematite iron oxide.



*Figure 2.* FTIR spectrum of  $\text{Fe}_2\text{O}_3$ -nanoparticles calcined at  $600^\circ\text{C}$ .

Figure 2 shows the FTIR spectrum of calcined iron oxide ( $\text{Fe}_2\text{O}_3$ ) particles. The FTIR peaks at 536 and  $467\text{ cm}^{-1}$  arise due to formation of iron oxygen bond (Fe-O).



*Figure 3.* FESEM image of  $\text{Fe}_2\text{O}_3$ -nanoparticles calcined at  $600^\circ\text{C}$ .

Figure 3 shows the FESEM image of the calcined iron oxide particles. As shown, the particles are not spherical and the widths of the particles are in nanometer dimension.

## 6. Analytical Data of Synthesized aza-Michael Addition Products 3aa-ai and 3ba, bg, ca, cg, ch, dg

### 3-(1*H*-Pyrazol-1-yl)cyclohexanone (**3aa**)<sup>1</sup> (Scheme 3):

**Condition A.** According to the general procedure reaction between cyclohex-2-en-1-one **1a** (1 mmol, 96 mg) and 1*H*-pyrazole **2a** (1 mmol, 68 mg) were carried out using P(NMe<sub>2</sub>)<sub>3</sub> (1.1 mmol, 197 mg) in acetonitrile to obtained the desired product **3aa** in 81% (133 mg) yield.

**Condition B.** According to the general procedure reaction between cyclohex-2-en-1-one **1a** (1 mmol, 96 mg) and 1*H*-pyrazole **2a** (1 mmol, 68 mg) were carried out using Fe<sub>2</sub>O<sub>3</sub>-NPs (0.1 mmol, 16 mg) in acetonitrile to obtained the desired product **3aa** in 77% (126 mg) yield.

Brown liquid; R<sub>f</sub> = 0.60 (SiO<sub>2</sub>, Hexane/EtOAc = 8:2); purification system: CombiFlash MPLC (Hexane/EtOAc = 80:20); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.54 (br, 1H), 7.4 (d, *J* = 1.2 Hz, 1H), 6.25 (br, 1H), 4.58-4.51 (m, 1H), 3.03-2.95 (dd, *J* = 14.5, 10.0 Hz, 1H), 2.85-2.8 (dd, *J* = 14.5, 5.0 Hz, 1H), 2.48-2.4 (m, 2H), 2.28-2.24 (m, 2H), 2.10-2.03 (m, 1H), 1.8-1.68 (m, 1H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 207.8, 139.3, 127.4, 105.3, 59.7, 47.6, 40.6, 31.7, 21.7 ppm; HRMS (EI-QTOF, [M + H]<sup>+</sup>): calculated for C<sub>9</sub>H<sub>13</sub>N<sub>2</sub>O: 165.1027; found: 165.1024.

### 3-(5-Methyl-1*H*-pyrazol-1-yl)cyclohexanone (**3ab**)<sup>1</sup> (Scheme 3):

**Condition A.** According to the general procedure reaction between cyclohex-2-en-1-one **1a** (1 mmol, 96 mg) and 5-methyl-1*H*-pyrazole **2b** (1 mmol, 82 mg) were carried out using P(NMe<sub>2</sub>)<sub>3</sub> (1.1 mmol, 197 mg) in acetonitrile to obtained the desired product **3ab** in 84% (150 mg) yield.

**Condition B.** According to the general procedure reaction between cyclohex-2-en-1-one **1a** (1 mmol, 96 mg) and 5-methyl-1*H*-pyrazole **2b** (1 mmol, 82 mg) were carried out using Fe<sub>2</sub>O<sub>3</sub>-NPs (0.1 mmol, 16 mg) in acetonitrile to obtained the desired product **3ab** in 86% (153 mg) yield.

Pale yellow liquid; R<sub>f</sub> = 0.60 (SiO<sub>2</sub>, Hexane/EtOAc = 8:2); purification system: CombiFlash MPLC (Hexane/EtOAc = 80:20); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.26 (d, *J* = 1.6 Hz, 1H), 6.0 (d, *J* = 1.6 Hz, 1H), 4.45-4.36 (dt, *J* = 14 Hz, 1H), 2.96 (dd, *J* = 14.0 Hz, 10.4 Hz, 1H), 2.8 (dd, *J* = 14.4 Hz, 5.0 Hz, 1H), 2.45 (t, *J* = 7.8 Hz, 1H), 2.27 (s, 3H), 2.23 (d, *J* = 4.8 Hz, 2H), 2.07-2.0 (m, 1H), 1.75-1.57 (m, 1H) ppm; HRMS (EI-QTOF, [M + H]<sup>+</sup>): calculated for C<sub>11</sub>H<sub>15</sub>N<sub>2</sub>O: 191.1184; found: 191.1181.

### 3-(3-(Trifluoromethyl)-1*H*-pyrazol-1-yl)cyclohexanone (**3ac**)<sup>1</sup> (Scheme 3):

**Condition A.** According to the general procedure reaction between cyclohex-2-en-1-one **1a** (1 mmol, 96 mg) and 3-(trifluoromethyl)-1*H*-pyrazole **2c** (1 mmol, 136 mg) were carried out using P(NMe<sub>2</sub>)<sub>3</sub> (1.1 mmol, 197 mg) in acetonitrile to obtained the desired product **3ac** in 82% (190 mg) yield.

**Condition B.** According to the general procedure reaction between cyclohex-2-en-1-one **1a** (1 mmol, 96 mg) and 3-(trifluoromethyl)-1*H*-pyrazole **2c** (1 mmol, 136 mg) were carried out using Fe<sub>2</sub>O<sub>3</sub>-NPs (0.1 mmol, 16 mg) in acetonitrile to obtained the desired product **3ac** in 85% (197 mg) yield.

Pale brown sticky liquid; R<sub>f</sub> = 0.60 (SiO<sub>2</sub>, Hexane/EtOAc = 8:2); purification system: CombiFlash MPLC (Hexane/EtOAc = 80:20); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.45 (d, *J* = 1.6 Hz, 1H), 6.5 (d, *J* = 1.6 Hz, 1H), 4.60-4.52 (m, 1H), 3.0 (dd, *J* = 14.0 Hz, 10.4 Hz, 1H), 2.87 (dd, *J* = 14.4 Hz, 4.8 Hz, 1H),

2.50-2.41 (m, 2H), 2.31-2.27 (m, 2H), 2.1-2.04 (m, 1H), 1.78-1.68 (m, 1H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 207.0, 142.5 (q, *J* = 38.0 Hz), 128.9, 121.2 (q, *J* = 267.3 Hz) 104.2, 60.6, 47.4, 40.4, 31.5, 21.6 ppm; HRMS (EI-QTOF, [M + H]<sup>+</sup>): calculated for C<sub>10</sub>H<sub>12</sub>F<sub>3</sub>N<sub>2</sub>O: 233.0901; found: 233.0900.

### 3-(4-Nitro-1*H*-pyrazol-1-yl)cyclohexanone (**3ad**)<sup>1</sup> (Scheme 3):

**Condition A.** According to the general procedure reaction between cyclohex-2-en-1-one **1a** (1 mmol, 96 mg) and 4-nitro-1*H*-pyrazole **2d** (1 mmol, 113 mg) were carried out using P(NMe<sub>2</sub>)<sub>3</sub> (1.1 mmol, 197 mg) in acetonitrile to obtained the desired product **3ad** in 52% (109 mg) yield.

**Condition B.** According to the general procedure reaction between cyclohex-2-en-1-one **1a** (1 mmol, 96 mg) and 4-nitro-1*H*-pyrazole **2d** (1 mmol, 113 mg) were carried out using Fe<sub>2</sub>O<sub>3</sub>-NPs (0.1 mmol, 16 mg) in acetonitrile to obtained the desired product **3ad** in 67% (140 mg) yield.

Grey Solid; R<sub>f</sub> = 0.60 (SiO<sub>2</sub>, Hexane/EtOAc = 8:2); purification system: CombiFlash MPLC (Hexane/EtOAc = 80:20); m.p = 131-133 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.48 (s, 1H), 6.9 (s, 1H), 4.6-4.53 (m, 1H), 3.02 (dd, *J* = 14.0 Hz, 10.4 Hz, 1H), 2.87 (dd, *J* = 14.4 Hz, 4.9 Hz, 1H), 2.51-2.4 (m, 2H), 2.4-2.32 (m, 2H), 2.16-2.07 (m, 1H), 1.8-1.57 (m, 1H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 206.2, 130.4, 102.8, 61.6, 47.1, 40.3, 31.4, 21.6 ppm; HRMS (EI-QTOF, [M + H]<sup>+</sup>): calculated for C<sub>9</sub>H<sub>12</sub>N<sub>3</sub>O<sub>3</sub>: 210.0878; found: 210.0873.

### Methyl 1-(3-oxocyclohexyl)-1*H*-pyrazole-3-carboxylate (**3ae**)<sup>1</sup> (Scheme 3):

**Condition A.** According to the general procedure reaction between cyclohex-2-en-1-one **1a** (1 mmol, 96 mg) and methyl 1*H*-pyrazole-3-carboxylate **2e** (1 mmol, 126 mg) were carried out using P(NMe<sub>2</sub>)<sub>3</sub> (1.1 mmol, 197 mg) in acetonitrile to obtained the desired product **3ae** in 52% (177 mg) yield.

**Condition B.** According to the general procedure reaction between cyclohex-2-en-1-one **1a** (1 mmol, 96 mg) and methyl 1*H*-pyrazole-3-carboxylate **2e** (1 mmol, 126 mg) were carried out using Fe<sub>2</sub>O<sub>3</sub>-NPs (0.1 mmol, 16 mg) in acetonitrile to obtained the desired product **3ae** in 67% (187 mg) yield.

Pale brown liquid; R<sub>f</sub> = 0.60 (SiO<sub>2</sub>, Hexane/EtOAc = 8:2); purification system: CombiFlash MPLC (Hexane/EtOAc = 80:20); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.43 (d, *J* = 2.0 Hz, 1H), 6.8 (d, *J* = 2.0 Hz, 1H), 4.6-4.53 (m, 1H), 3.9 (s, 3H), 3.02 (dd, *J* = 14.4 Hz, 10.0 Hz, 1H), 2.85 (dd, *J* = 14.0 Hz, 5.0 Hz, 1H), 2.47-2.38 (m, 2H), 2.3-2.26 (m, 2H), 2.1-2.03 (m, 1H), 1.78-1.66 (m, 1H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 207.1, 162.6, 143.6, 128.9, 108.9, 60.9, 52.0, 47.5, 40.4, 31.6, 21.8 ppm; HRMS (EI-QTOF, [M + H]<sup>+</sup>): calculated for C<sub>11</sub>H<sub>15</sub>N<sub>2</sub>O<sub>3</sub>: 223.1082; found: 223.1078.

### Methyl 1-(3-oxocyclohexyl)-1*H*-1,2,4-triazole-3-carboxylate (**3af**)<sup>1</sup> (Scheme 3):

**Condition A.** According to the general procedure reaction between cyclohex-2-en-1-one **1a** (1 mmol, 96 mg) and methyl 1*H*-1,2,4-triazole-3-carboxylate **2f** (1 mmol, 127 mg) were carried out using P(NMe<sub>2</sub>)<sub>3</sub> (1.1 mmol, 197 mg) in acetonitrile to obtained the desired product **3af** in 76% (180 mg) yield.

**Condition B.** According to the general procedure reaction between cyclohex-2-en-1-one **1a** (1 mmol, 96 mg) and methyl 1*H*-1,2,4-triazole-3-carboxylate **2f** (1 mmol, 127 mg) were carried out using Fe<sub>2</sub>O<sub>3</sub>-NPs (0.1 mmol, 16 mg) in acetonitrile to obtained the desired product **3ae** in 73% (173 mg) yield.

White solid; R<sub>f</sub> = 0.5 (SiO<sub>2</sub>, Hexane/EtOAc = 8:2); purification system: CombiFlash MPLC (Hexane/EtOAc = 80:20); mp = 124-125 °C (Lit<sup>1</sup> mp = 122.4-123.6 °C); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ = 8.74 (s, 1H), 4.94-4.87 (m, 1H), 3.86 (s, 3H), 2.94 (dd, *J* = 12.0 Hz, 8.0 Hz, 1H), 2.75

(dd,  $J = 12.0$  Hz, 4.0 Hz, 1H), 2.49-2.42 (m, 1H), 2.33-2.27 (m, 1H), 2.24-2.09 (m, 2H), 2.01-1.93 (m, 1H), 1.77-1.66 (m, 1H) ppm;  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta = 206.8, 159.8, 153.6, 144.7, 57.6, 52.1, 46.3, 30.3, 20.9$  ppm; HRMS (EI-QTOF,  $[\text{M} + \text{H}]^+$ ): calculated for  $\text{C}_{10}\text{H}_{14}\text{N}_3\text{O}_3$ : 224.1035; found: 224.1032.

### **3-(1H-Indazol-1-yl)cyclohexanone (3ag)<sup>1</sup>** (Scheme 3):

**Condition A.** According to the general procedure reaction between cyclohex-2-en-1-one **1a** (1 mmol, 96 mg) and 1H-indazole **2g** (1 mmol, 118 mg) were carried out using  $\text{P}(\text{NMe}_2)_3$  (1.1 mmol, 197 mg) in acetonitrile to obtain the desired product **3ag** in 78% (167 mg) yield.

**Condition B.** According to the general procedure reaction between cyclohex-2-en-1-one **1a** (1 mmol, 96 mg) and 1H-indazole **2g** (1 mmol, 118 mg) were carried out using  $\text{Fe}_2\text{O}_3$ -NPs (0.1 mmol, 16 mg) in acetonitrile to obtain the desired product **3ag** in 81% (174 mg) yield.

Brown liquid;  $R_f = 0.60$  ( $\text{SiO}_2$ , Hexane/EtOAc = 8:2); purification system: CombiFlash MPLC (Hexane/EtOAc = 80:20);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.02$  (s, 1H), 7.73 (d,  $J = 8.0$  Hz, 1H), 7.41-7.36 (m, 2H), 7.62 (dt,  $J = 8.6$  Hz, 1H), 4.91-4.84 (m, 1H), 3.18 (dd,  $J = 12.0$  Hz, 8.0 Hz, 1H), 2.79 (dd,  $J = 12.0$  Hz, 4.0 Hz, 1H), 2.51-2.47 (m, 2H), 2.41-2.31 (m, 1H), 2.25-2.18 (m, 1H), 2.14-2.05 (m, 1H), 1.83-1.71 (m, 1H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 208.3, 138.6, 133.3, 126.3, 124.0, 121.2, 121.1, 120.8, 108.5, 56.1, 47.1, 40.7, 30.8, 21.9$  ppm; HRMS (EI-QTOF,  $[\text{M} + \text{H}]^+$ ): calculated for  $\text{C}_{13}\text{H}_{15}\text{N}_2\text{O}$ : 215.1184; found: 215.1180.

### **Methyl 1-(3-oxocyclohexyl)-1H-indazole-3-carboxylate (3ah)<sup>1</sup>** (Scheme 3):

**Condition A.** According to the general procedure reaction between cyclohex-2-en-1-one **1a** (1 mmol, 96 mg) and methyl 1H-indazole-3-carboxylate **2h** (1 mmol, 176 mg) were carried out using  $\text{P}(\text{NMe}_2)_3$  (1.1 mmol, 197 mg) in acetonitrile to obtain the desired product **3ah** in 77% (210 mg) yield.

**Condition B.** According to the general procedure reaction between cyclohex-2-en-1-one **1a** (1 mmol, 96 mg) and methyl 1H-indazole-3-carboxylate **2h** (1 mmol, 176 mg) were carried out using  $\text{Fe}_2\text{O}_3$ -NPs (0.1 mmol, 16 mg) in acetonitrile to obtain the desired product **3ah** in 74% (201 mg) yield.

Pale yellow solid;  $R_f = 0.55$  ( $\text{SiO}_2$ , Hexane/EtOAc = 8:2); purification system: CombiFlash MPLC (Hexane/EtOAc = 80:20); mp = 90-92 °C (Lit<sup>1</sup> mp = 91.8-92.6 °C);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.23$  (d,  $J = 8.0$  Hz, 1H), 7.49-7.43 (m, 2H), 7.33 (dt,  $J = 8.0$  Hz, 1H), 4.91-4.84 (m, 1H), 4.03 (s, 3H), 3.30 (t,  $J = 12.0$  Hz, 1H), 2.83 (dd,  $J = 12.0$  Hz, 4.0 Hz, 1H), 2.56-2.43 (m, 3H), 2.30-2.16 (m, 2H), 1.84-1.73 (m, 1H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 207.5, 162.9, 139.7, 135.3, 127.0, 123.7, 123.4, 122.4, 109.1, 52.2, 52.1, 47.2, 40.5, 30.9, 22.1$  ppm; HRMS (EI-QTOF,  $[\text{M} + \text{H}]^+$ ): calculated for  $\text{C}_{15}\text{H}_{17}\text{N}_2\text{O}_3$ : 273.1239; found: 273.1236.

### **3-(4-Bromo-1H-indazol-1-yl)cyclohexanone (3ai)<sup>1</sup>** (Scheme 3):

**Condition A.** According to the general procedure reaction between cyclohex-2-en-1-one **1a** (1 mmol, 96 mg) and 4-bromo-1H-indazole **2i** (1 mmol, 197 mg) were carried out using  $\text{P}(\text{NMe}_2)_3$  (1.1 mmol, 197 mg) in acetonitrile to obtain the desired product **3ai** in 79% (232 mg) yield.

**Condition B.** According to the general procedure reaction between cyclohex-2-en-1-one **1a** (1 mmol, 96 mg) and 4-bromo-1H-indazole **2i** (1 mmol, 197 mg) were carried out using  $\text{Fe}_2\text{O}_3$ -NPs (0.1 mmol, 16 mg) in acetonitrile to obtain the desired product **3ai** in 83% (243 mg) yield.

Brown solid;  $R_f = 0.6$  ( $\text{SiO}_2$ , Hexane/EtOAc = 8:2); purification system: CombiFlash MPLC (Hexane/EtOAc = 80:20); mp = 89-90 °C (Lit<sup>1</sup> mp = 87.1-88.0 °C);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.02$  (s, 1H), 7.35-7.30 (m, 2H), 7.22 (t,  $J = 8.0$  Hz, 1H), 4.86-4.79 (m, 1H), 3.17 (dd,  $J = 12.0$  Hz,

8.0 Hz, 1H), 2.78 (dd,  $J = 12.0$  Hz, 4.0 Hz 1H), 2.51-2.47 (m, 2H), 2.42-2.31 (m, 1H), 2.25-2.18 (m, 1H), 2.15-2.07 (m, 1H), 1.85-1.71 (m, 1H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 207.9, 139.1, 133.5, 127.1, 125.1, 123.7, 114.8, 107.6, 56.6, 47.06, 40.6, 30.8, 21.8$  ppm; HRMS (EI-QTOF,  $[\text{M} + \text{H}]^+$ ): calculated for  $\text{C}_{13}\text{H}_{14}\text{BrN}_2\text{O}$ : 293.0289; found: 293.0285.

### 3-(1*H*-Pyrazol-1-yl)cyclopentanone (3ba)<sup>1</sup> (Scheme 4):

**Condition A.** According to the general procedure reaction between cyclopent-2-en-1-one **1b** (1 mmol, 82 mg) and 1*H*-pyrazole **2a** (1 mmol, 68 mg) were carried out using  $\text{P}(\text{NMe}_2)_3$  (1.1 mmol, 197 mg) in acetonitrile to obtain the desired product **3ba** in 82% (229 mg) yield.

**Condition B.** According to the general procedure reaction between cyclopent-2-en-1-one **1a** (1 mmol, 96 mg) and 1*H*-pyrazole **2a** (1 mmol, 68 mg) were carried out using  $\text{Fe}_2\text{O}_3$ -NPs (0.1 mmol, 16 mg) in acetonitrile to obtain the desired product **3ba** in 85% (237 mg) yield.

Pale brown sticky liquid;  $R_f = 0.60$  ( $\text{SiO}_2$ , Hexane/EtOAc = 8:2); purification system: CombiFlash MPLC (Hexane/EtOAc = 80:20);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.53$  (d,  $J = 3.2$  Hz, 1H), 7.44 (d,  $J = 4.0$  Hz, 1H), 6.26 (t,  $J = 4.0$  Hz, 1H), 4.99-4.93 (m, 1H), 2.86-2.69 (m, 2H), 2.65-2.39 (m, 2H), 2.36-2.27 (m, 1H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 215.1, 139.6, 127.9, 105.6, 58.5, 44.7, 36.9, 30.3$  ppm; HRMS (EI-QTOF,  $[\text{M} + \text{H}]^+$ ): calculated for  $\text{C}_8\text{H}_{11}\text{N}_2\text{O}$ : 151.0871; found: 151.0866.

### 3-(1*H*-Indazol-1-yl)cyclopentanone (3bg)<sup>1</sup> (Scheme 4):

**Condition A.** According to the general procedure reaction between cyclopent-2-en-1-one **1b** (1 mmol, 82 mg) and 1*H*-indazole **2g** (1 mmol, 118 mg) were carried out using  $\text{P}(\text{NMe}_2)_3$  (1.1 mmol, 197 mg) in acetonitrile to obtain the desired product **3bg** in 86% (136 mg) yield.

**Condition B.** According to the general procedure reaction between cyclohex-2-en-1-one **1a** (1 mmol, 96 mg) and 1*H*-indazole **2g** (1 mmol, 118 mg) were carried out using  $\text{Fe}_2\text{O}_3$ -NPs (0.1 mmol, 16 mg) in acetonitrile to obtain the desired product **3bg** in 83% (166 mg) yield.

Brown sticky liquid;  $R_f = 0.60$  ( $\text{SiO}_2$ , Hexane/EtOAc = 8:2); purification system: CombiFlash MPLC (Hexane/EtOAc = 80:20);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.99$  (s, 1H), 7.74 (d,  $J = 8.0$  Hz, 1H), 7.46-7.38 (m, 2H), 7.17 (t,  $J = 8.6$  Hz, 1H), 5.34-5.28 (m, 1H), 2.97 (dd,  $J = 16.0$  Hz, 4.0 Hz, 1H), 2.77 (dd,  $J = 20.0$  Hz, 8.0 Hz, 1H), 2.71-2.62 (m, 1H), 2.58-2.47 (m, 2H), 2.40-2.32 (m, 1H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 215.6, 139.0, 133.3, 126.3, 124.3, 121.3, 120.8, 108.6, 55.0, 44.1, 36.7, 29.6$  ppm; HRMS (EI-QTOF,  $[\text{M} + \text{H}]^+$ ): calculated for  $\text{C}_{12}\text{H}_{13}\text{N}_2\text{O}$ : 201.1027; found: 201.1022.

### 3-(1*H*-Pyrazol-1-yl)cycloheptanone (3ca)<sup>1</sup> (Scheme 4):

**Condition A.** According to the general procedure reaction between cyclohept-2-en-1-one **1c** (1 mmol, 110 mg) and 1*H*-pyrazole **2a** (1 mmol, 68 mg) were carried out using  $\text{P}(\text{NMe}_2)_3$  (1.1 mmol, 197 mg) in acetonitrile to obtain the desired product **3ca** in 79% (141 mg) yield.

**Condition B.** According to the general procedure reaction between cyclohept-2-en-1-one **1c** (1 mmol, 110 mg) and 1*H*-pyrazole **2a** (1 mmol, 68 mg) were carried out using  $\text{Fe}_2\text{O}_3$ -NPs (0.1 mmol, 16 mg) in acetonitrile to obtain the desired product **3ca** in 87% (155 mg) yield.

Sticky liquid;  $R_f = 0.60$  ( $\text{SiO}_2$ , Hexane/EtOAc = 8:2); purification system: CombiFlash MPLC (Hexane/EtOAc = 80:20);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.50$  (d,  $J = 3.2$  Hz, 1H), 7.38 (d,  $J = 3.8$  Hz, 1H), 6.24 (t,  $J = 4.0$  Hz, 1H), 4.48 (tt,  $J = 12.0$  Hz, 1H), 3.28 (dd,  $J = 16.0$  Hz, 12.0 Hz, 1H), 2.85 (td,  $J = 8.0$  Hz, 1H), 2.67-2.6 (m, 1H), 2.55-2.48 (m, 1H), 2.27-2.12 (m, 2H), 2.07-1.94 (m, 1H), 1.82-1.72 (m, 2H), 1.61-1.51 (m, 1H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 210.4, 139.1, 127.1, 105.4, 58.7, 50.2, 44.0, 37.7, 26.5, 23.6$  ppm; HRMS (EI-QTOF,  $[\text{M} + \text{H}]^+$ ): calculated for  $\text{C}_{10}\text{H}_{15}\text{N}_2\text{O}$ : 179.1184; found: 179.1180.

### 3-(1*H*-Indazol-1-yl)cycloheptanone (**3cg**)<sup>1</sup> (Scheme 4):

**Condition A.** According to the general procedure reaction between cyclohept-2-en-1-one **1c** (1 mmol, 110 mg) and 1*H*-indazole **2g** (1 mmol, 118 mg) were carried out using P(NMe<sub>2</sub>)<sub>3</sub> (1.1 mmol, 197 mg) in acetonitrile to obtained the desired product **3cg** in 76% (176 mg) yield.

**Condition B.** According to the general procedure reaction between cyclohept-2-en-1-one **1c** (1 mmol, 110 mg) and 1*H*-indazole **2g** (1 mmol, 118 mg) were carried out using Fe<sub>2</sub>O<sub>3</sub>-NPs (0.1 mmol, 16 mg) in acetonitrile to obtained the desired product **3cg** in 79% (180 mg) yield.

Pale yellow Solid; R<sub>f</sub> = 0.60 (SiO<sub>2</sub>, Hexane/EtOAc = 8:2); purification system: CombiFlash MPLC (Hexane/EtOAc = 80:20); mp = 93 - 95 °C (Lit<sup>1</sup> mp = 91.4 - 92.4 °C); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.90 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.27 (t, *J* = 8.0 Hz, 1H), 7.07 (t, *J* = 8.0 Hz, 1H), 4.76-4.68 (m, 1H), 3.45 (dd, *J* = 16.0 Hz, 12.0 Hz, 1H), 2.94 (dd, *J* = 12.0 Hz, 4.0 Hz, 1H), 2.81-2.64 (m, 1H), 2.58-2.5 (m, 1H), 2.36-2.31 (m, 2H), 2.12-1.97 (m, 2H), 1.86-1.75 (m, 1H), 1.64-1.53 (m, 1H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 209.7, 148.6, 126.0, 121.7, 121.4, 120.7, 120.1, 117.4, 60.5, 50.4, 44.0, 38.2, 26.6, 23.6 ppm; HRMS (EI-QTOF, [M + H]<sup>+</sup>): calculated for C<sub>14</sub>H<sub>17</sub>N<sub>2</sub>O: 229.1340; found: 229.1331.

### Methyl 1-(3-oxocycloheptyl)-1*H*-indazole-3-carboxylate (**3ch**)<sup>1</sup> (Scheme 4):

**Condition A.** According to the general procedure reaction between cyclohept-2-en-1-one **1c** (1 mmol, 110 mg) and methyl 1*H*-indazole-3-carboxylate **2h** (1 mmol, 176 mg) were carried out using P(NMe<sub>2</sub>)<sub>3</sub> (1.1 mmol, 197 mg) in acetonitrile to obtained the desired product **3ch** in 74% (212 mg) yield.

**Condition B.** According to the general procedure reaction between cyclohept-2-en-1-one **1c** (1 mmol, 110 mg) and methyl 1*H*-indazole-3-carboxylate **2h** (1 mmol, 176 mg) were carried out using Fe<sub>2</sub>O<sub>3</sub>-NPs (0.1 mmol, 16 mg) in acetonitrile to obtained the desired product **3ch** in 78% (233 mg) yield.

Grey solid; R<sub>f</sub> = 0.6 (SiO<sub>2</sub>, Hexane/EtOAc = 8:2); purification system: CombiFlash MPLC (Hexane/EtOAc = 80:20); mp = 92-95 °C (Lit<sup>1</sup> mp = 95.4-96.2 °C); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 8.01 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.28 (t, *J* = 8.0 Hz, 1H), 6.05-5.98 (m, 1H), 4.03 (s, 3H), 3.52 (dd, *J* = 16.0 Hz, 12.0 Hz, 1H), 2.91 (dd, *J* = 12.0 Hz, 4.0 Hz, 1H), 2.76-2.59 (m, 2H), 2.37-2.3 (m, 2H), 2.1-1.98 (m, 2H), 1.87-1.76 (m, 1H), 1.74-1.64 (m, 1H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 210.2, 160.7, 147.4, 126.3, 125.2, 123.2, 122.7, 121.4, 118.3, 58.3, 52.0, 50.2, 44.1, 38.2, 27.0, 23.9 ppm; HRMS (EI-QTOF, [M + H]<sup>+</sup>): calculated for C<sub>16</sub>H<sub>19</sub>N<sub>2</sub>O<sub>3</sub>: 287.1395; found: 287.1392.

### 4-(1*H*-Indazol-1-yl)butan-2-one (**3dg**)<sup>1</sup> (Scheme 4):

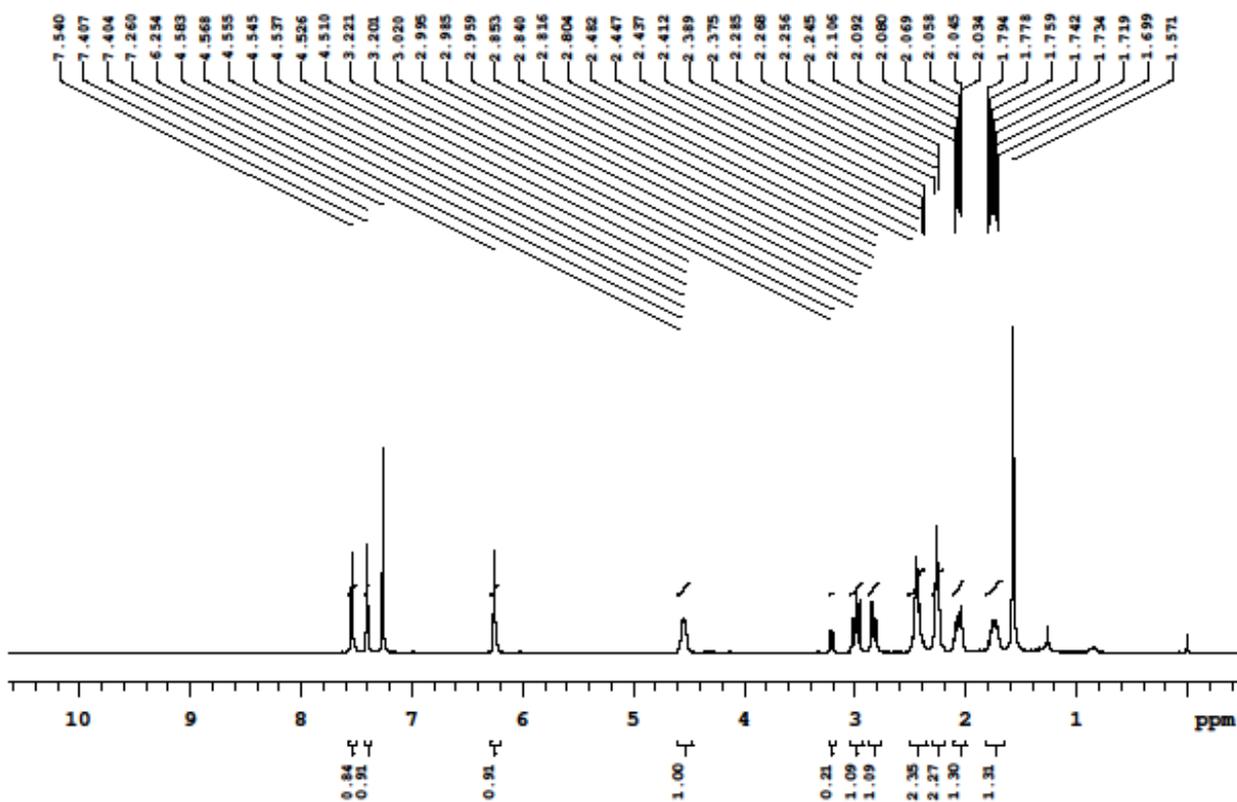
**Condition A.** According to the general procedure reaction between but-3-en-2-one **1d** (1 mmol, 70 mg) and 1*H*-indazole **2g** (1 mmol, 118 mg) were carried out using P(NMe<sub>2</sub>)<sub>3</sub> (1.1 mmol, 197 mg) in acetonitrile to obtained the desired product **3dg** in 77% (189 mg) yield.

**Condition B.** According to the general procedure reaction between but-3-en-2-one **1d** (1 mmol, 70 mg) and 1*H*-indazole **2g** (1 mmol, 118 mg) were carried out using Fe<sub>2</sub>O<sub>3</sub>-NPs (0.1 mmol, 16 mg) in acetonitrile to obtained the desired product **3dg** in 83% (204 mg) yield.

Pale yellow stick liquid; R<sub>f</sub> = 0.40 (SiO<sub>2</sub>, Hexane/EtOAc = 8:2); purification system: CombiFlash MPLC (Hexane/EtOAc = 80:20); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.97 (s, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.26 (t, *J* = 8.0 Hz, 1H), 7.05 (t, *J* = 8.0 Hz, 1H), 4.67 (t, *J* = 8.0 Hz, 2H), 3.19 (t, *J* = 8.0 Hz, 2H), 2.13 (s, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 205.5, 149.0, 125.9,

123.8, 121.5, 120.2, 117.1, 47.6, 43.3, 30.1 ppm; HRMS (EI-QTOF,  $[M + H]^+$ ): calculated for  $C_{11}H_{13}N_2O$ : 189.1027; found: 189.1023.

### 7. NMR Spectral Data



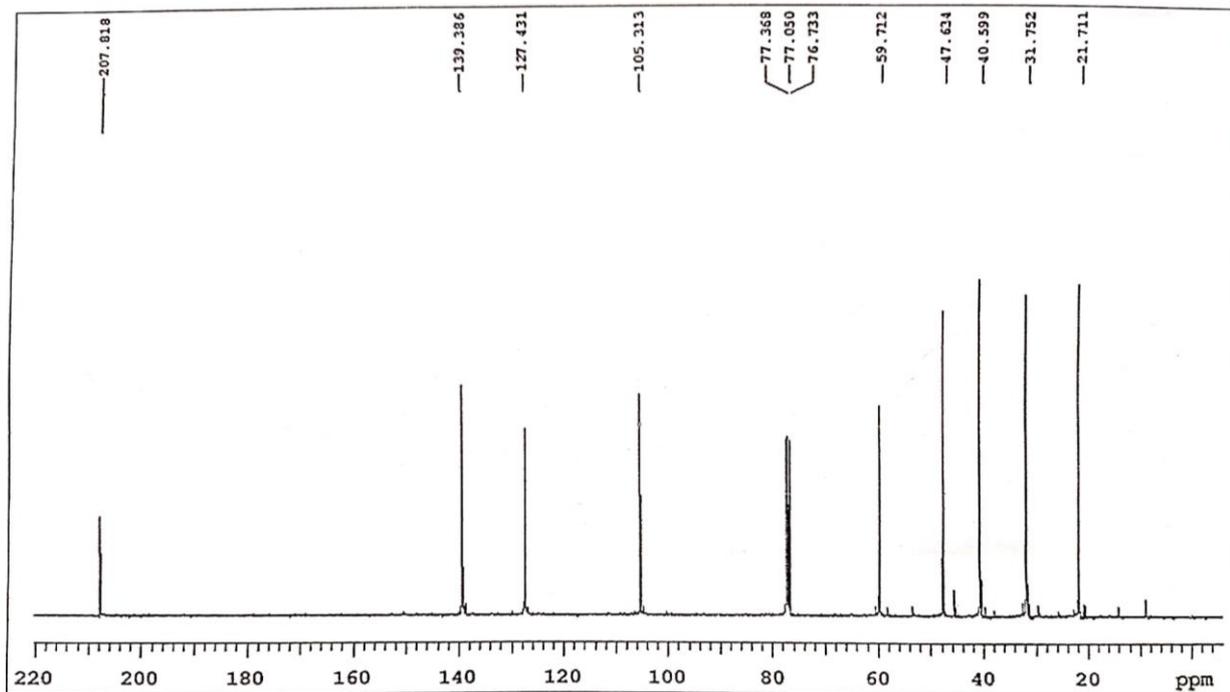


Figure 4.  $^1\text{H}$  (400 MHz),  $^{13}\text{C}$  (100 MHz) NMR spectra of **3aa** in  $\text{CDCl}_3$ .

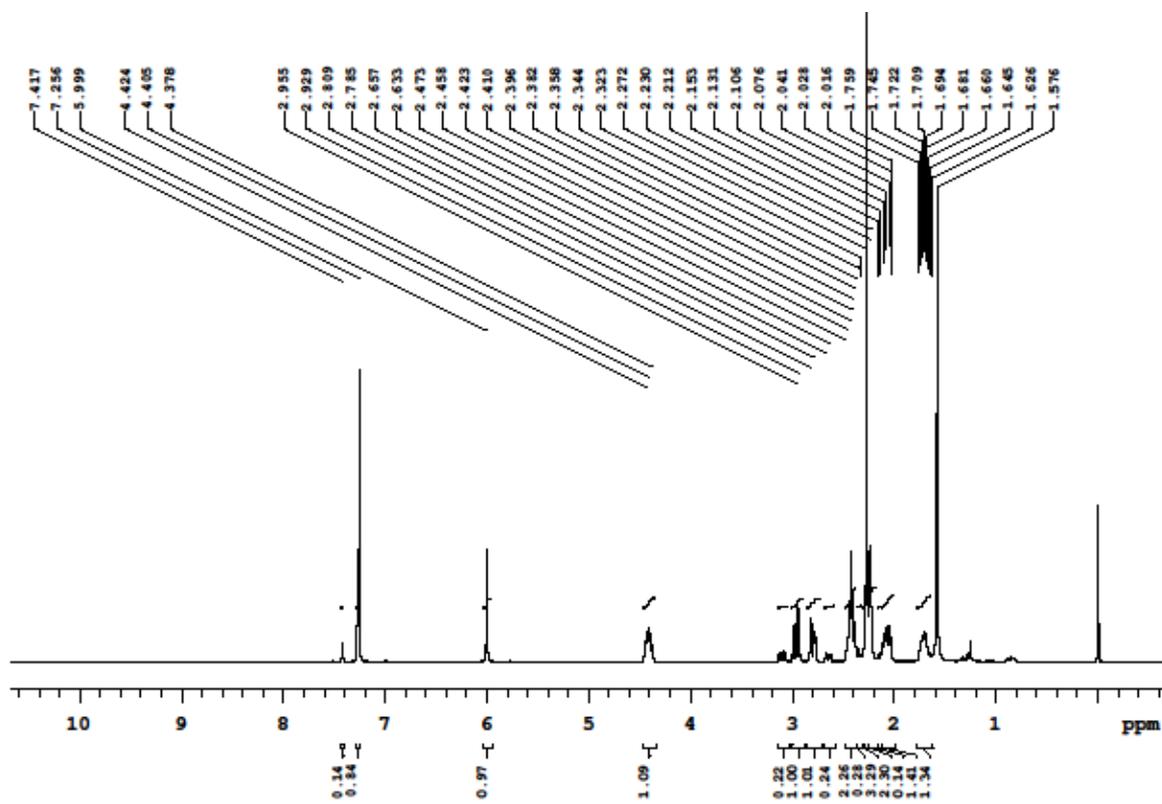


Figure 5.  $^1\text{H}$  (400 MHz) NMR spectra of **3ab** in  $\text{CDCl}_3$ .

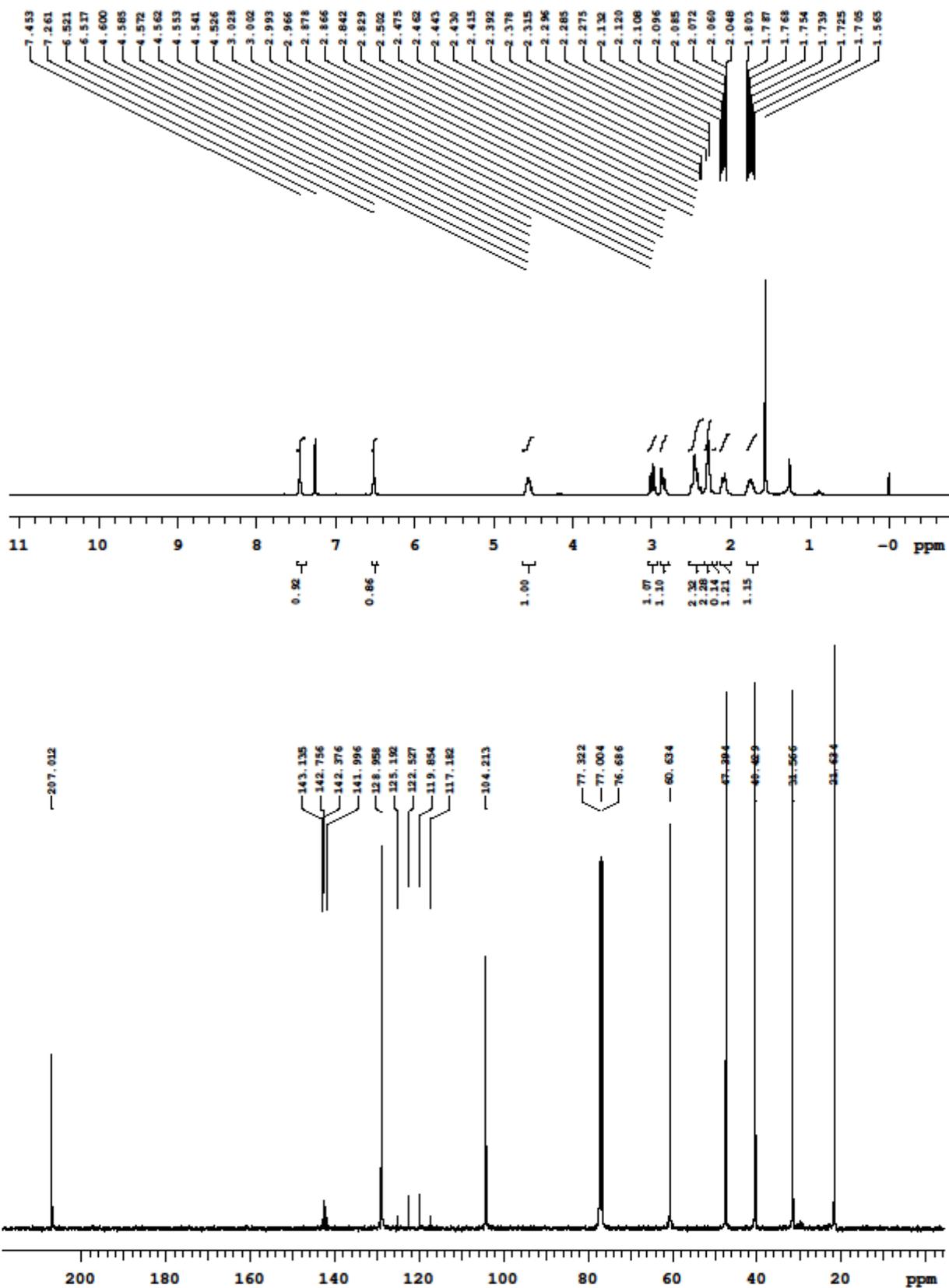


Figure 6.  $^1\text{H}$  (400 MHz),  $^{13}\text{C}$  (100 MHz) NMR spectra of **3ac** in  $\text{CDCl}_3$ .

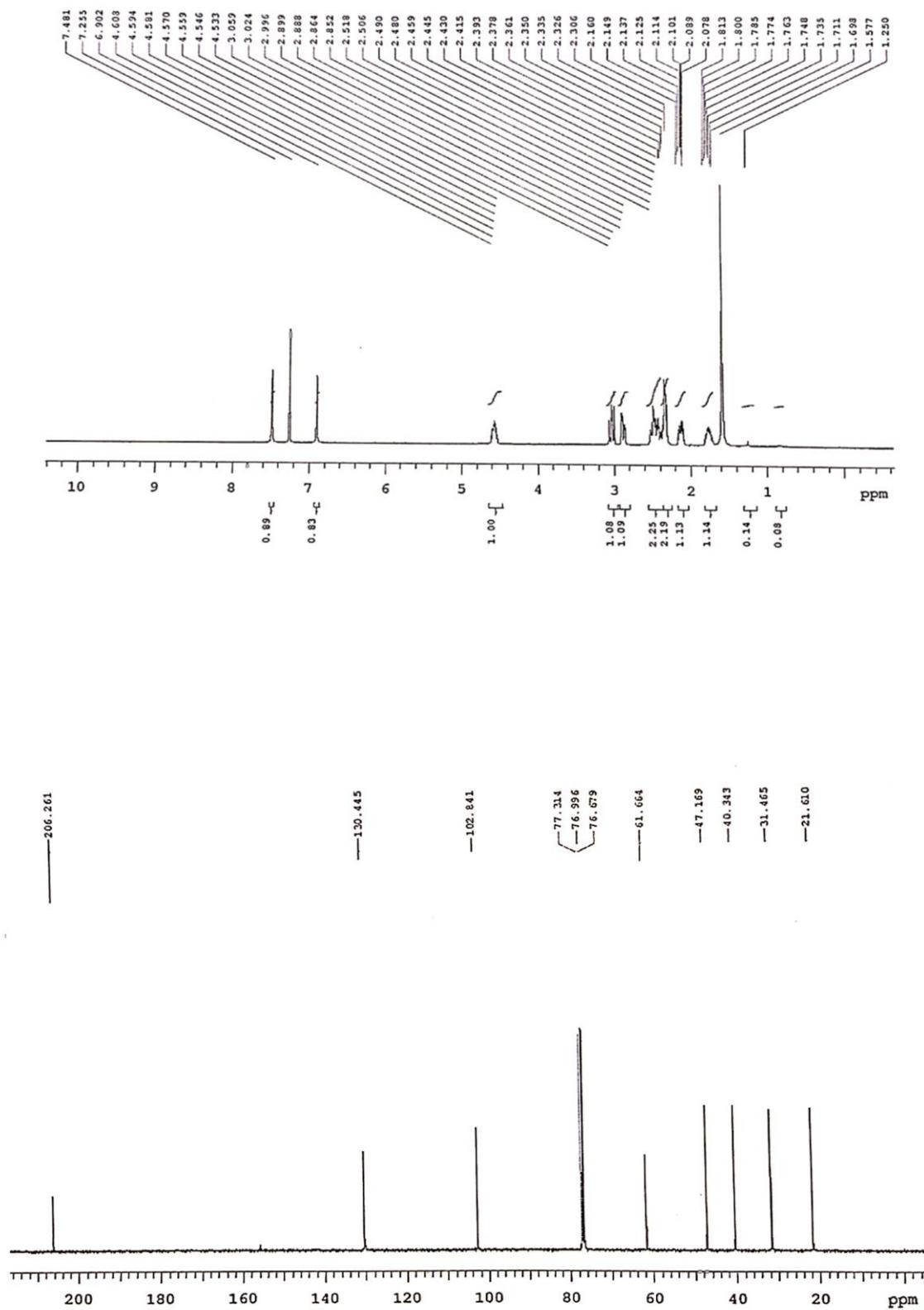


Figure 7.  $^1\text{H}$  (400 MHz),  $^{13}\text{C}$  (100 MHz) NMR spectra of **3ad** in  $\text{CDCl}_3$ .

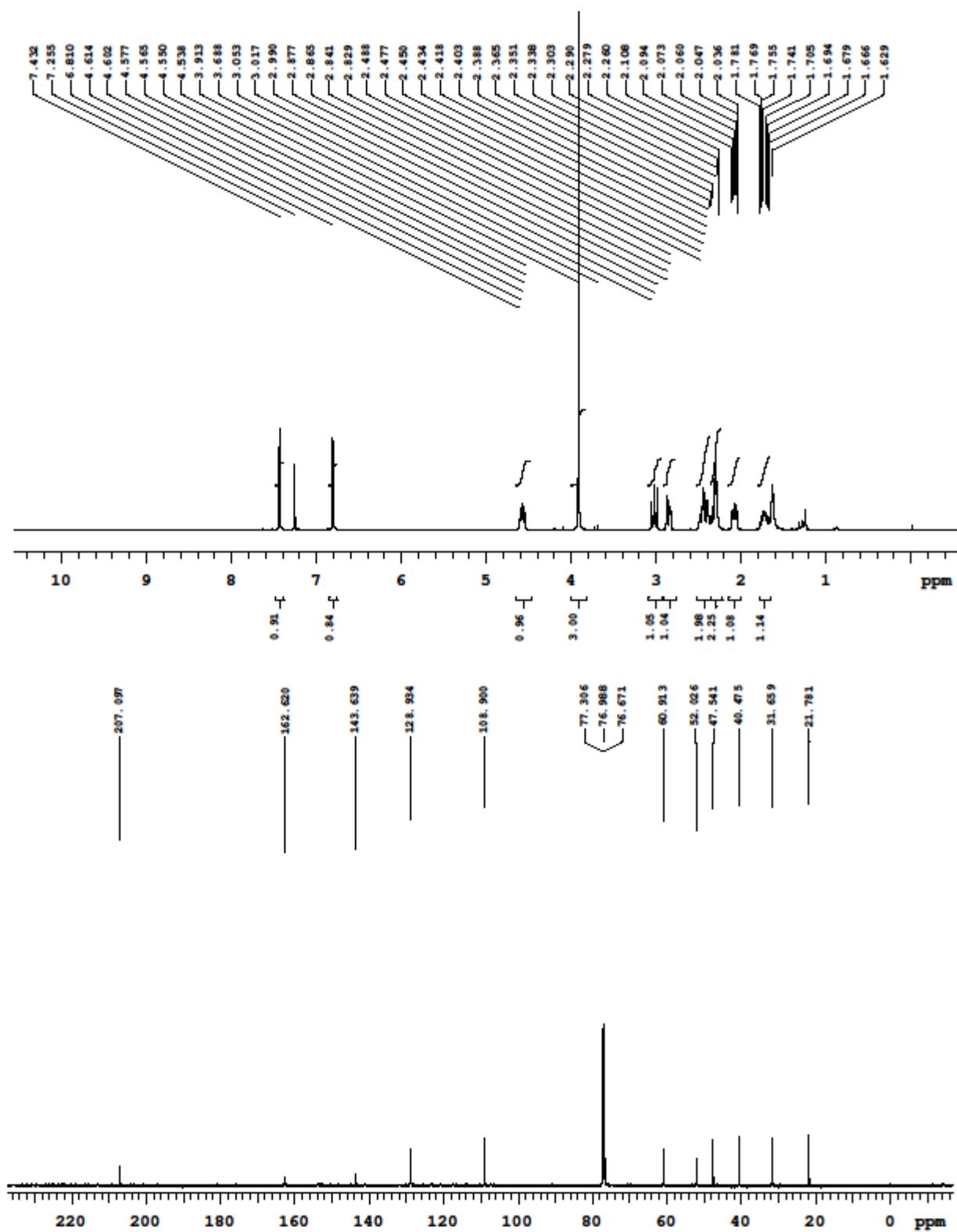
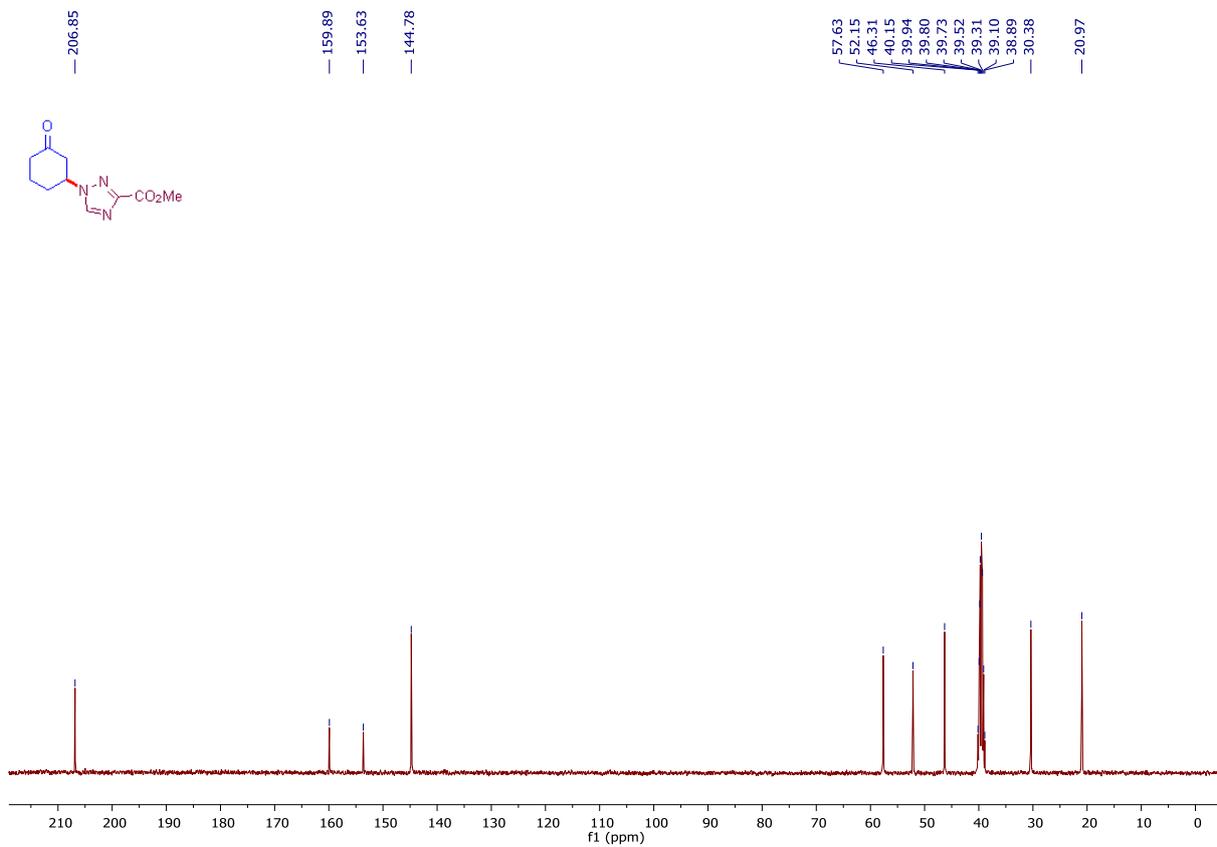
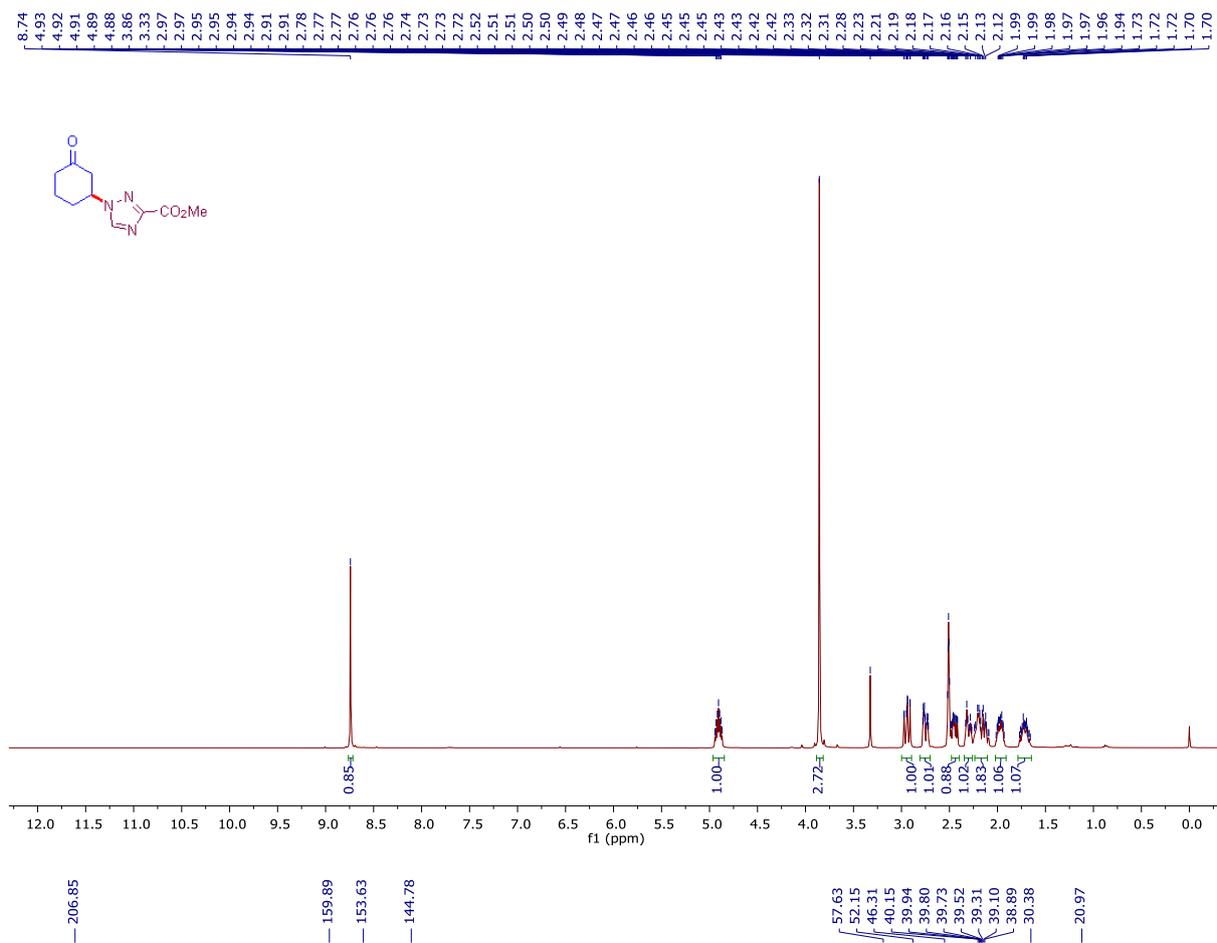


Figure 8.  $^1\text{H}$  (400 MHz),  $^{13}\text{C}$  (100 MHz) NMR spectra of **3ae** in  $\text{CDCl}_3$ .



**Figure 9.** <sup>1</sup>H (400 MHz), <sup>13</sup>C (100 MHz) NMR spectra of **3af** in DMSO-*d*<sub>6</sub>.

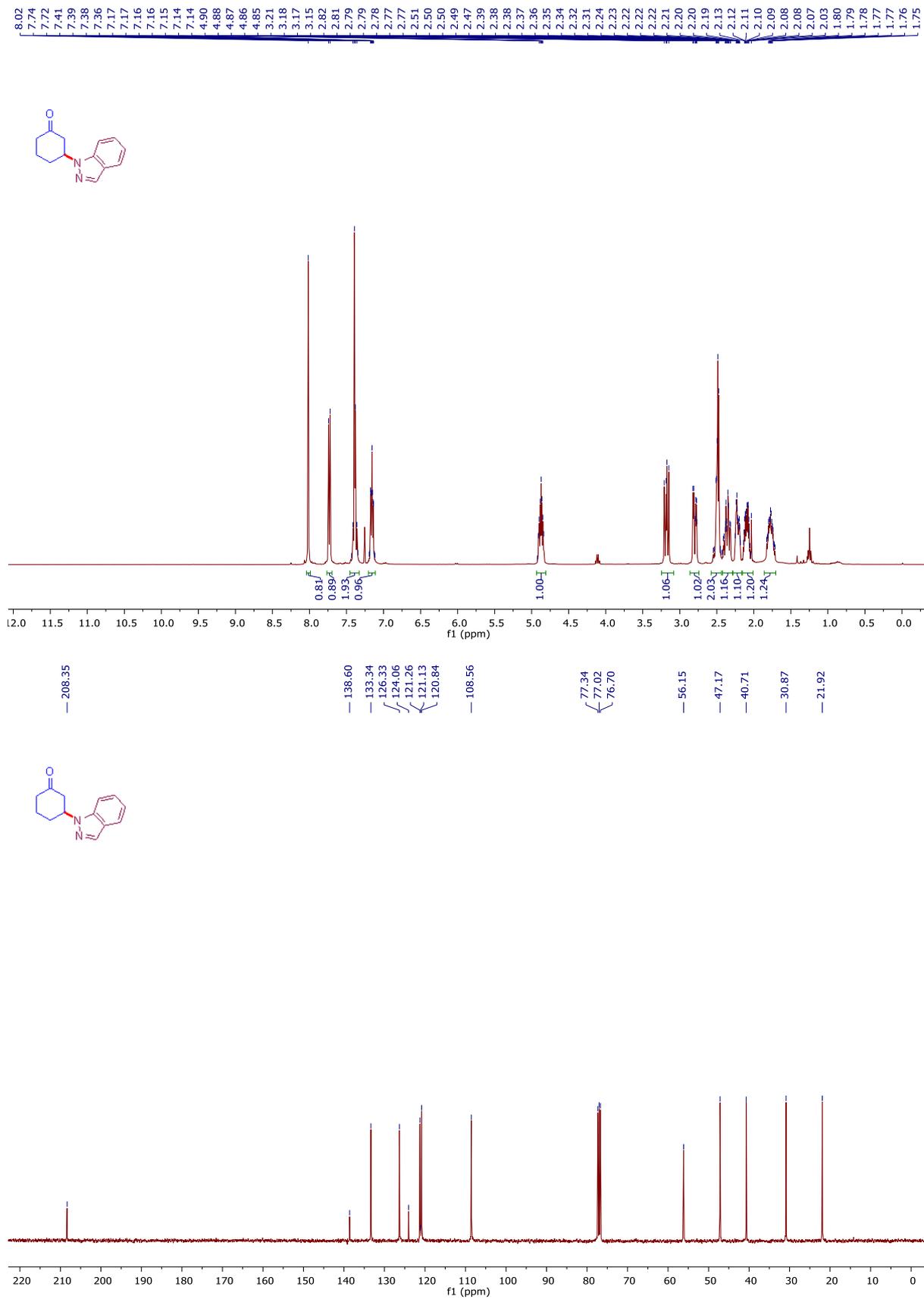


Figure 10. <sup>1</sup>H (400 MHz), <sup>13</sup>C (100 MHz) NMR spectra of **3ag** in CDCl<sub>3</sub>.

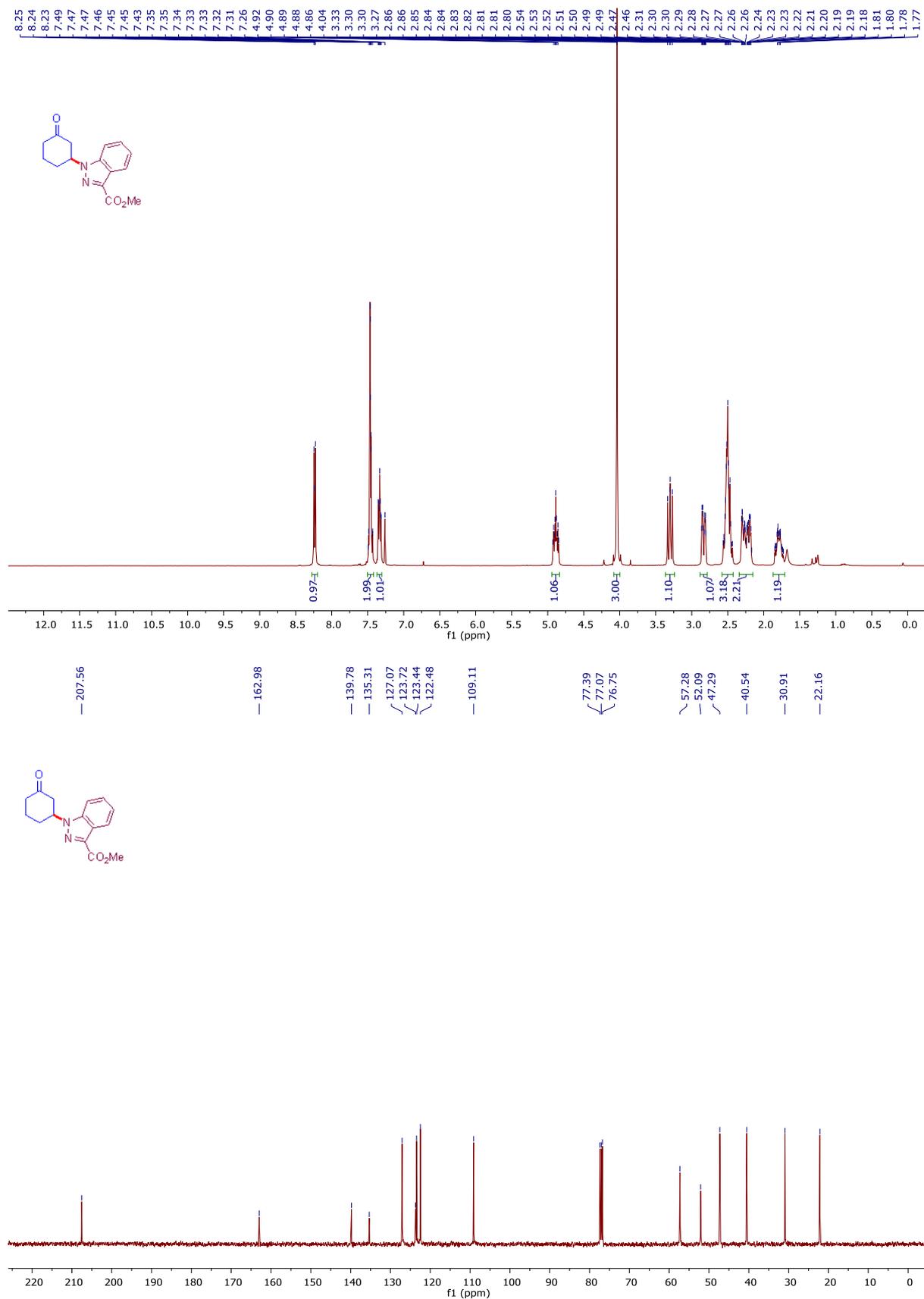


Figure 11. <sup>1</sup>H (400 MHz), <sup>13</sup>C (100 MHz) NMR spectra of **3ah** in CDCl<sub>3</sub>.

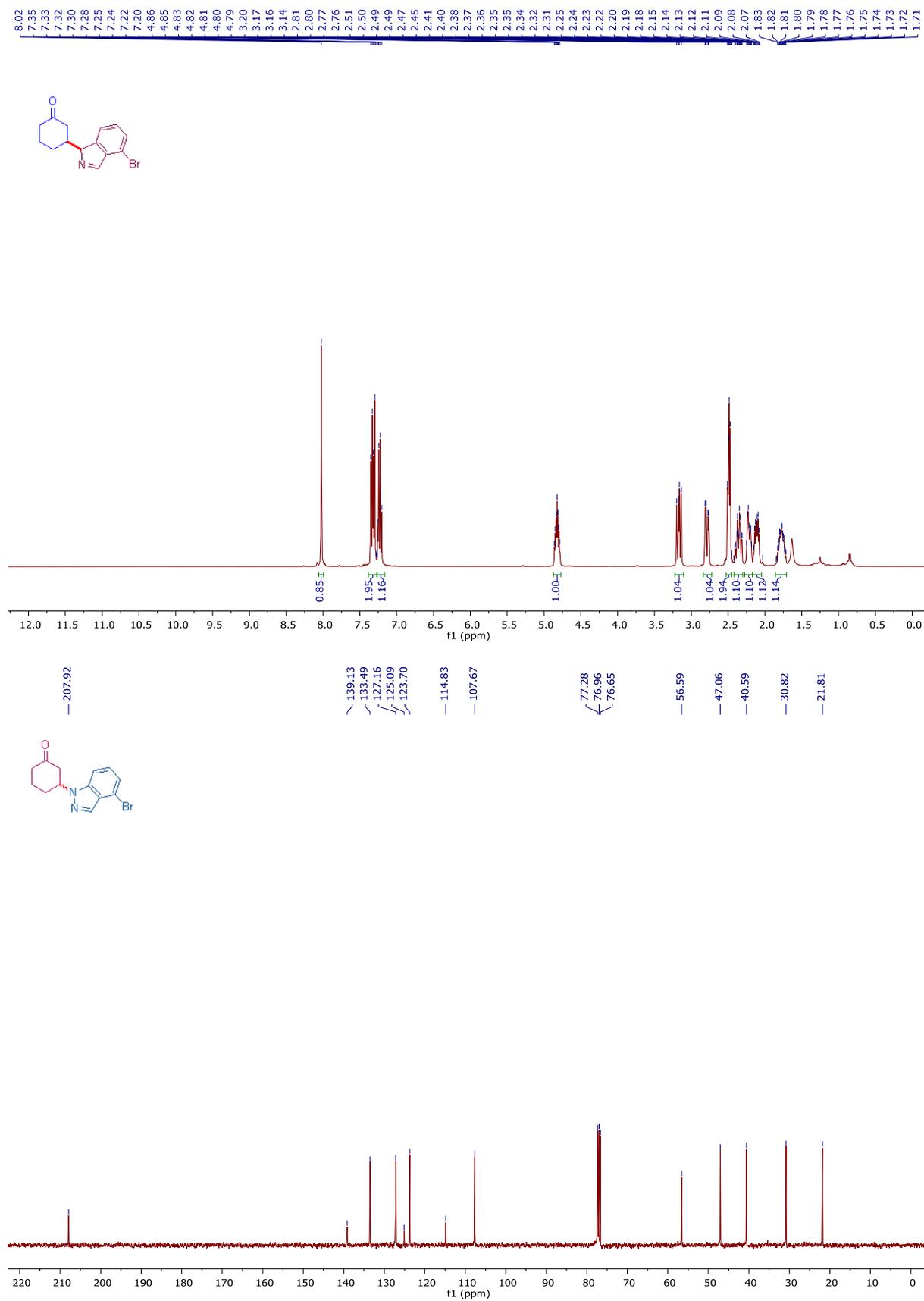


Figure 12. <sup>1</sup>H (400 MHz), <sup>13</sup>C (100 MHz) NMR spectra of **3ai** in CDCl<sub>3</sub>.

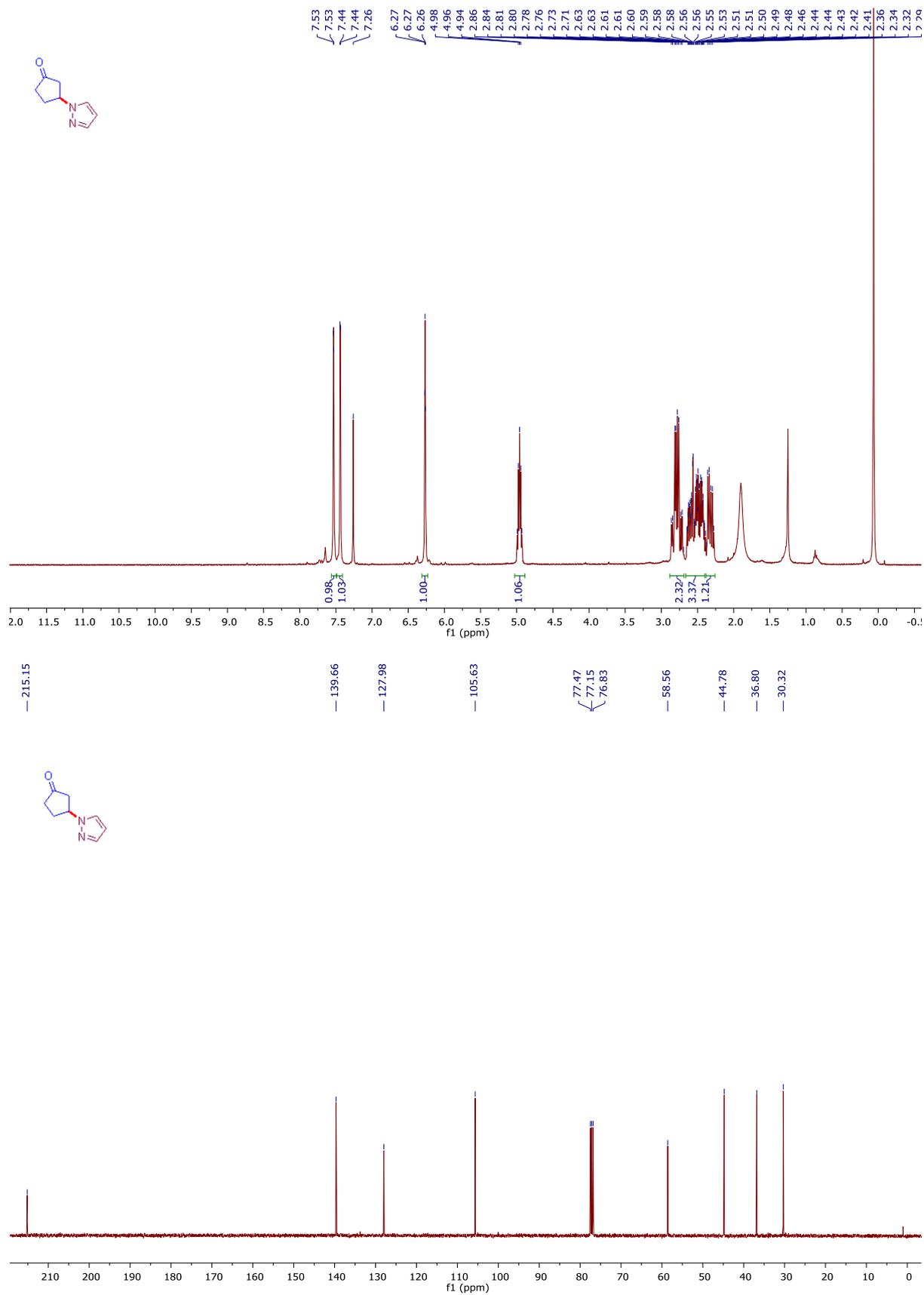


Figure 13. <sup>1</sup>H (400 MHz), <sup>13</sup>C (100 MHz) NMR spectra of **3ba** in CDCl<sub>3</sub>.

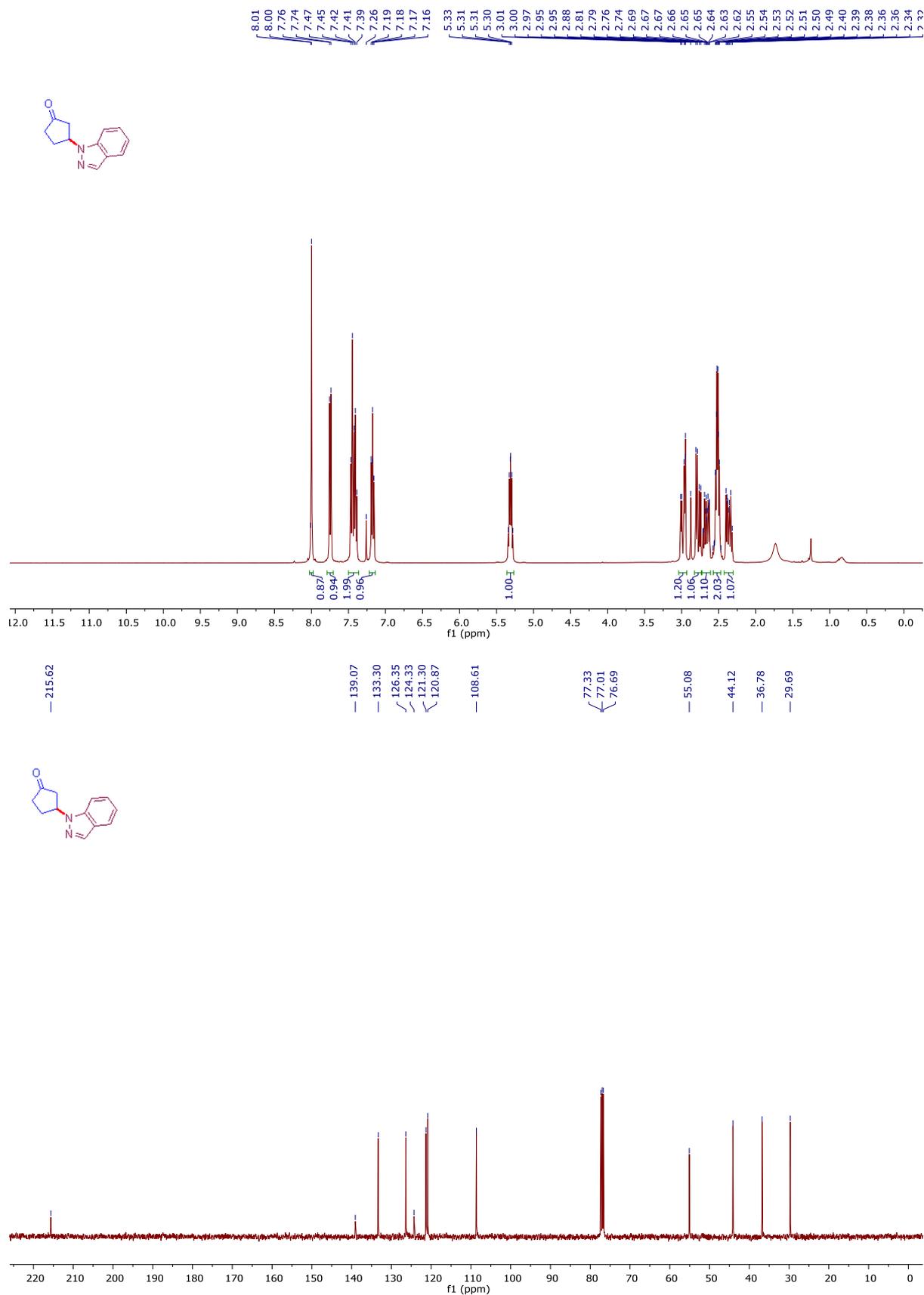


Figure 14. <sup>1</sup>H (400 MHz), <sup>13</sup>C (100 MHz) NMR spectra of **3bg** in CDCl<sub>3</sub>.

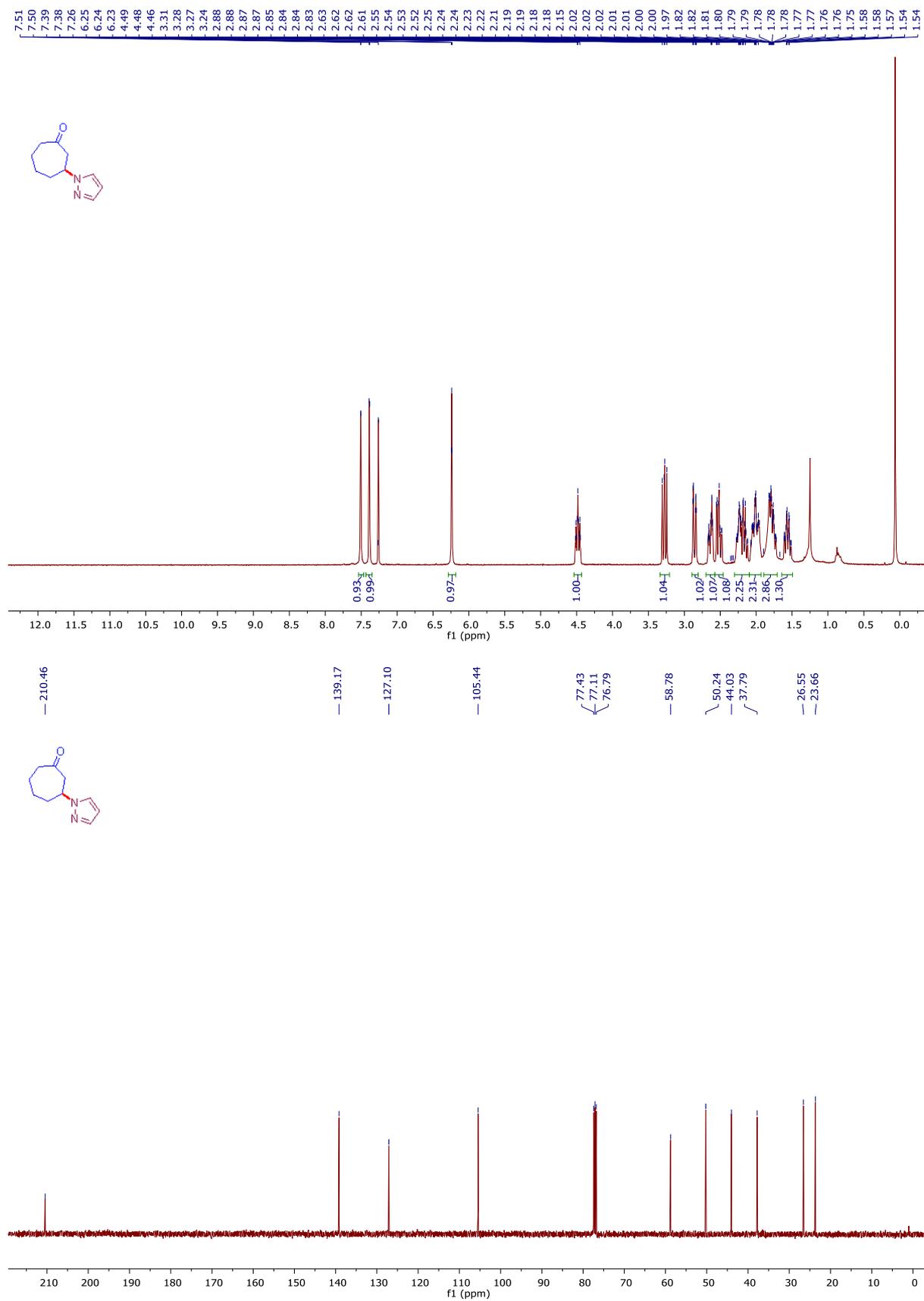


Figure 15. <sup>1</sup>H (400 MHz), <sup>13</sup>C (100 MHz) NMR spectra of **3ca** in CDCl<sub>3</sub>.

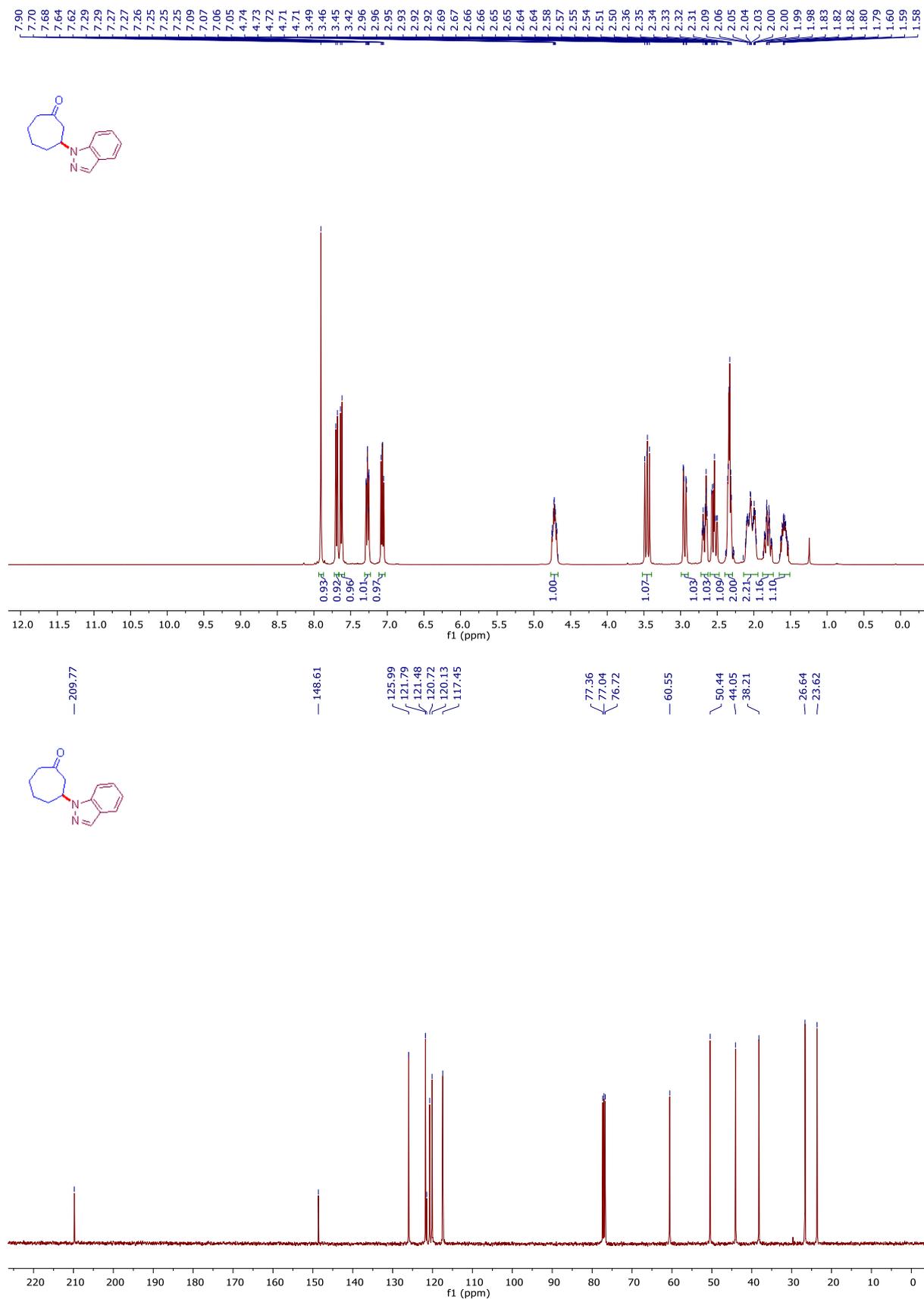


Figure 16. <sup>1</sup>H (400 MHz), <sup>13</sup>C (100 MHz) NMR spectra of **3cg** in CDCl<sub>3</sub>.

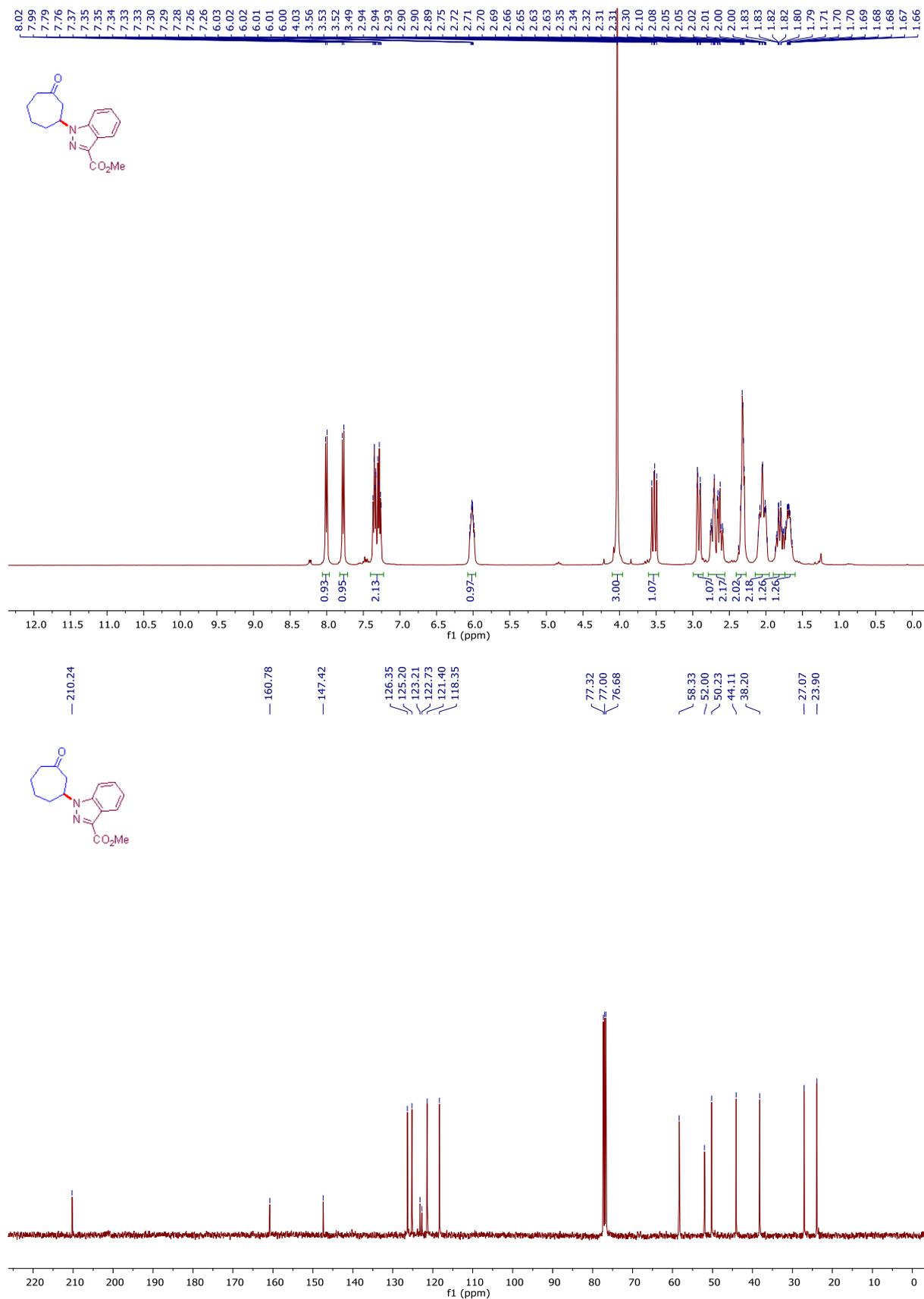


Figure 17. <sup>1</sup>H (400 MHz), <sup>13</sup>C (100 MHz) NMR spectra of **3ch** in CDCl<sub>3</sub>.

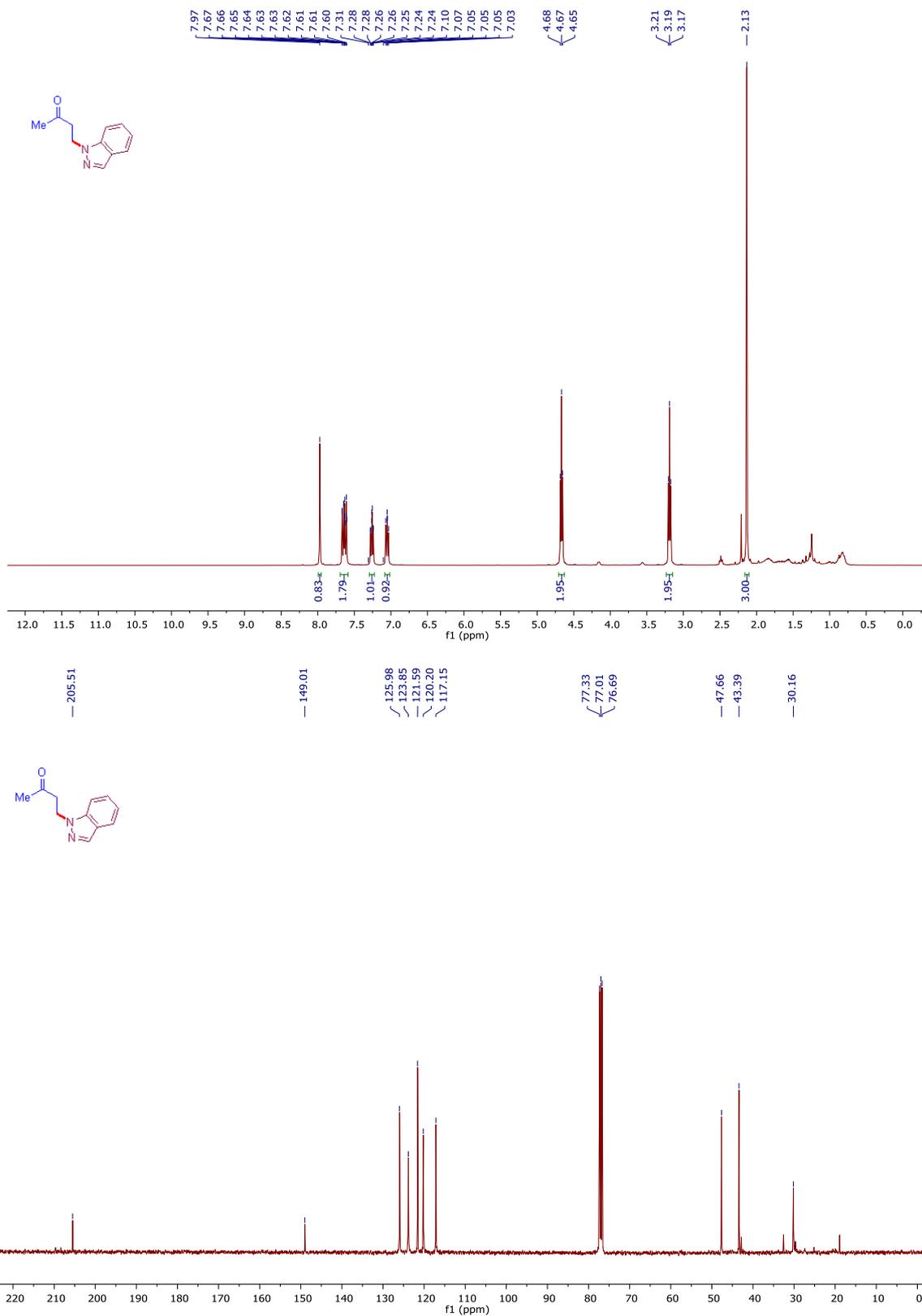


Figure 18. <sup>1</sup>H (400 MHz), <sup>13</sup>C (100 MHz) NMR spectra of **3dg** in CDCl<sub>3</sub>.

## Reference

1. S. Polina, V. P. R. K. Putta, R. Gujjarappa, P. P. Pujar, and C. C. Malakar, *J. Heterocyclic Chem.*, 2021, **58**, 1029.