

# Supporting Information

## Utilization of CO<sub>2</sub> for Production of Cyclic $\beta$ -Triketone Type Insecticides

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This supporting information contains 44 pages, 12 figures, and 5 tables.

## Table of Contents:

### Experimental section

#### Figures:

Figure S1. A summary of organic chemicals produced from CO<sub>2</sub> utilization.

Figure S2. The step-by-step tracking of the reaction of CO<sub>2</sub> with **1a** through <sup>1</sup>H NMR (dmf-*d*7 as solvent). The slash boxes in different colours assign the peak positions of corresponding hydrogen atoms, respectively. The ratios of enol and ketone in the solvent are given by the integrations of corresponding peaks.

Figure S3. <sup>1</sup>H NMR spectrum of **1a** in dmf-*d*7.

Figure S4. <sup>1</sup>H NMR spectrum of (**1a** + Cs<sub>2</sub>CO<sub>3</sub>) in dmf-*d*7.

Figure S5. <sup>13</sup>C NMR spectrum of (**1a** + Cs<sub>2</sub>CO<sub>3</sub>) in dmf-*d*7.

Figure S6. <sup>1</sup>H NMR spectrum of (**1a** + Cs<sub>2</sub>CO<sub>3</sub> + CuI) with dmf-*d*7 as solvent.

Figure S7. <sup>1</sup>H NMR spectrum of **1a** after reaction 24 h in dmf-*d*7.

Figure S8. A ball-and-stick diagram of **2a**.

Figure S9. A ball-and-stick diagram of **2b**.

Figure S10. A ball-and-stick diagram of CsHCO<sub>3</sub>.

Figure S11. A ball-and-stick diagram of C<sub>24</sub>H<sub>42</sub>Cs<sub>4</sub>O<sub>15</sub> (**1a-Cs**).

Figure S12. A ball-and-stick diagram of **3a**.

#### Tables:

Table S1. Isolated Yield of **3a-3e**.

Table S2. Isolated Yield of **4a-4e** from **2**.

Table S3. Isolated Yield of **4a-4e** from **3**.

Table S4. Insecticidal Activity of Compound **3a-3e**.

Table S5. Crystallographic data and structure refinements.

### NMR data for all products

#### <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra

## Experimental section

### General information

Unless otherwise noted, all manipulations were performed under a dry argon or carbon dioxide atmosphere using Schlenk-line techniques or under an argon atmosphere in an Mbraun glovebox. All the reagents employed were commercially available and used without further purification. IR spectra were recorded with a Bruker Vector 22. NMR spectra were recorded on a Bruker Ascend-400 spectrometer ( $^1\text{H}$  NMR, 400 MHz;  $^{13}\text{C}$  NMR, 101 MHz). High resolution EI mass experiments were operated on a Varian 7.0T FTMSinstrument. SXRD experiments were operated on a Bruker Smart 1000, Oxford SuperNova TM. Data were reported in the following order: chemical shift in ppm (multiplicity was indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet)). The crystallographic information was analyzed by X-ray diffraction (XRD, Ultima IV) equipped with a Cu  $K\alpha$  radiation source.

### General experimental procedure for 1,3-Cyclohexanedione-2-acid and derivatives (2a-2e)

The 1,3-Cyclohexanedione and derivatives (1.0 mmol) **1a-1e**,  $\text{Cs}_2\text{CO}_3$  (489 mg, 1.5 mmol) and CuI (19 mg) or CuBr (14 mg) were placed in a 10 mL Schlenk reaction tube. The reaction tube was degassed, and the  $\text{CO}_2$  (balloon) and DMF (5.0 mL) were introduced in to the reaction mixture under stirring. Afterwards, the reaction mixture was stirred at 50 °C for 48 h, then the resulting mixture was cooled to room temperature. Water (20 mL) was added to dissolve the reaction solid mixture. Then the solution was acidified with concentrated HCl to pH = 1 and stirred for 0.5 h. The  $\beta$ -tricarboxyl acid was extracted with

CH<sub>2</sub>Cl<sub>2</sub>. The organic phase was dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was evaporated under vacuum. The product was purified by a column chromatography (EAC:PE = 3:1) and characterized by NMR.

### **General experimental procedure for 3a-3e**

The synthesis of **3a-3e** is improved according to the methods of literature.<sup>[1]</sup> Dissolve 1,3-Cyclohexanedione-2-acid and derivatives **2** (1.0 mmol) into THF (10 mL), added 2.1 times equivalent of SOCl<sub>2</sub>, added two drops of DMF, reflux at 60 °C for 1 h, cool to room temperature, and remove the solvent and excess of SOCl<sub>2</sub> under reduced pressure. The reduced pressure product was dissolved in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> solution, then dropwise the solution into 10 mL CH<sub>2</sub>Cl<sub>2</sub> solution contain 2 equivalents of aniline (2.0 mmol), two drops of triethylamine were added, and the mixture was reacted at room temperature for 2 h. After the reaction, the solvent was removed under pressure, 20 mL of distilled water was added, and extracted three times with CH<sub>2</sub>Cl<sub>2</sub>. Anhydrous magnesium sulfate was added, after 0.5 h, the mixture was filtered. The solvent was removed under reduced pressure and the residue was purified by column chromatography (EAC:PE = 1:9). Obtained the target compound **3a-3e**.

### **General experimental procedure for 4a-4e (Path A)**

The synthesis of **4a-4e** is improved according to the methods of literature.<sup>[2]</sup> Dissolve 1,3-Cyclohexanedione-2-acid and derivatives **2a-2e** (1.0 mmol) into toluene (30 mL), added 5 times equivalent of DCC (5.0 mmol, 1.0 g), then dropwise the aniline (1.5 mmol, 140 mg), and the mixture was reacted at 110 °C for overnight. After the reaction, the solvent

was removed under pressure, 20 mL of distilled water was added, added HCl to the pH=2, and extracted three times with ethyl acetate. Anhydrous magnesium sulfate was added, after 0.5 h, the mixture was filtered. The solvent was removed under reduced pressure and the residue was purified by column chromatography (EAC:PE = 1:9). Obtained the target compound **4a-4e**.

### **General experimental procedure for 4a-4e (Path B)**

The synthesis of **4a-4e** is improved according to the methods of literature.<sup>[3]</sup> **3a-3e** (100 mg) in concentrated H<sub>2</sub>SO<sub>4</sub> (6.0 mL) was diluted with an equal volume of water and brought to 80 °C reflux for 12 h. The product was poured into 50 mL water, extracted with CH<sub>2</sub>Cl<sub>2</sub>, dried by anhydrous magnesium sulfate, filtered, the solvent was removed under reduced pressure and the residue was purified by column chromatography (EAC:PE = 1:3). Obtained the target compound **4a-4e**.

### **Single crystal X-ray diffraction study**

Crystallographic data of **2a**, **2b**, **3a**, C<sub>24</sub>H<sub>42</sub>Cs<sub>4</sub>O<sub>15</sub> and CsHCO<sub>3</sub> were collected on an Agilent Technologies SuperNova Single Crystal Diffractometer at 120 K or 150 K equipped with graphite-monochromatic Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Absorption corrections were applied by using the multiscan program. All the structures were solved by direct methods with SHELXS and refined with the full-matrix least-squares technique using the SHELXL program contained on Olex 2<sup>[4-5]</sup>. All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were generated geometrically. Crystal data as well as details of data collection and refinement for the complexes are summarized in Supplementary Tables S5. CCDC: 1955775-1955778, 1980055, contains the

supplementary crystallographic data for this paper, which can be obtained free of charge from the Cambridge Crystallographic Data Center.

### ***Mythimna separata* walker killing activity test**

*Mythimna separata* walker used in the test is a normal population, which is raised indoors. The test was carried out with the Leaf-dipping method. A corn leaf was immersed in an acetone solution containing selected insecticide ( $600 \mu\text{g ml}^{-1}$ ). Then the prepared dipped leaf was contacted to the 4th instar larvae via mainly stomach poisoning and contact toxicity, by the same time the feeding phenomenon of the larva was followed. The mortality rate was checked and recorded by 24 h.

### ***Culex pipiens pallens* killing activity test**

*Culex pipiens pallens* used in the test is a normal population kept indoors. About 5.0 mg of the test compound was weighed into a penicillin vial, and 5.0 mL of acetone (or a suitable solvent) was added to obtain  $1000 \mu\text{gml}^{-1}$  of mother liquor. 0.5 mL of the mother liquor was pipetted and added in a 100 mL beaker with 39.9 mL water. Ten 4th instar mosquito larvae were selected, and were poured together with the feed solution (10 mL) into the beaker above. The final concentration of the solution in the beaker is thus  $10 \mu\text{gml}^{-1}$ . The killing result was checked by 24 h in a standard treatment room. An aqueous solution containing 0.5 mL of the test solvent was used as a blank.

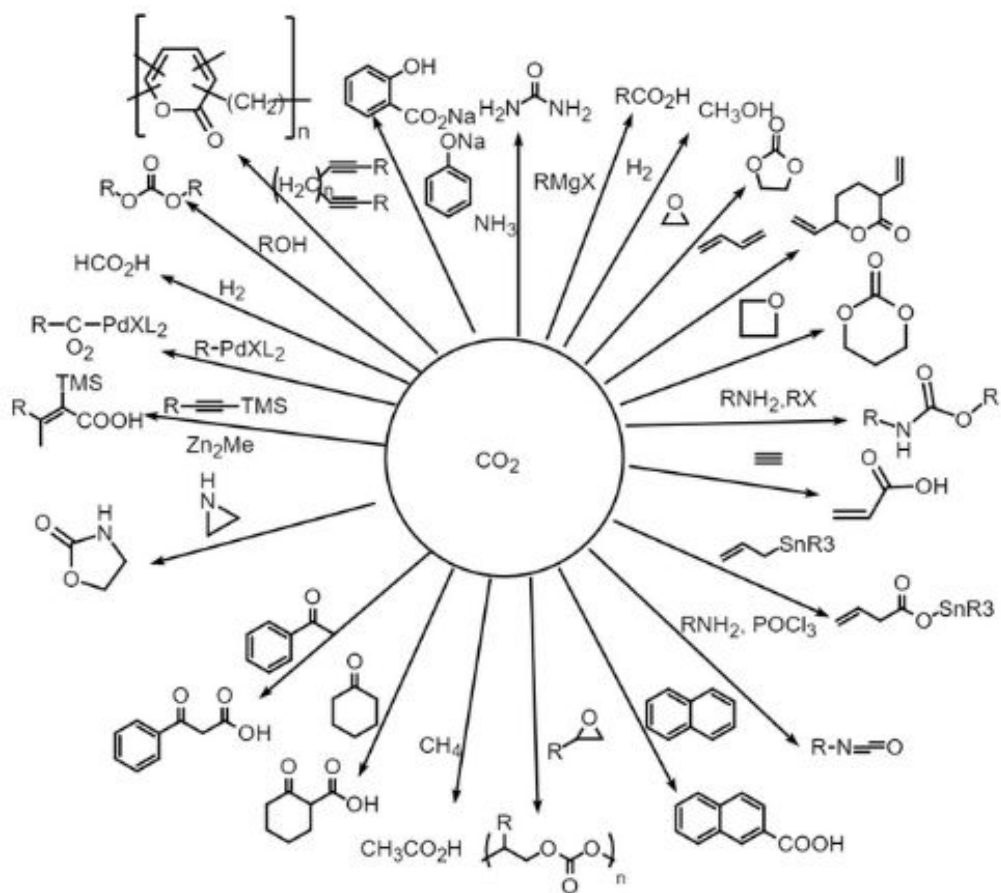
### ***Helicoverpa armigera* killing activity test**

*Helicoverpa armigera*, a normal population raised indoors. Test method: leaf dipping method. Dipping leaf method, using corn leaf soaked in acetone solution (600 ppm, 600 mg/L). After the

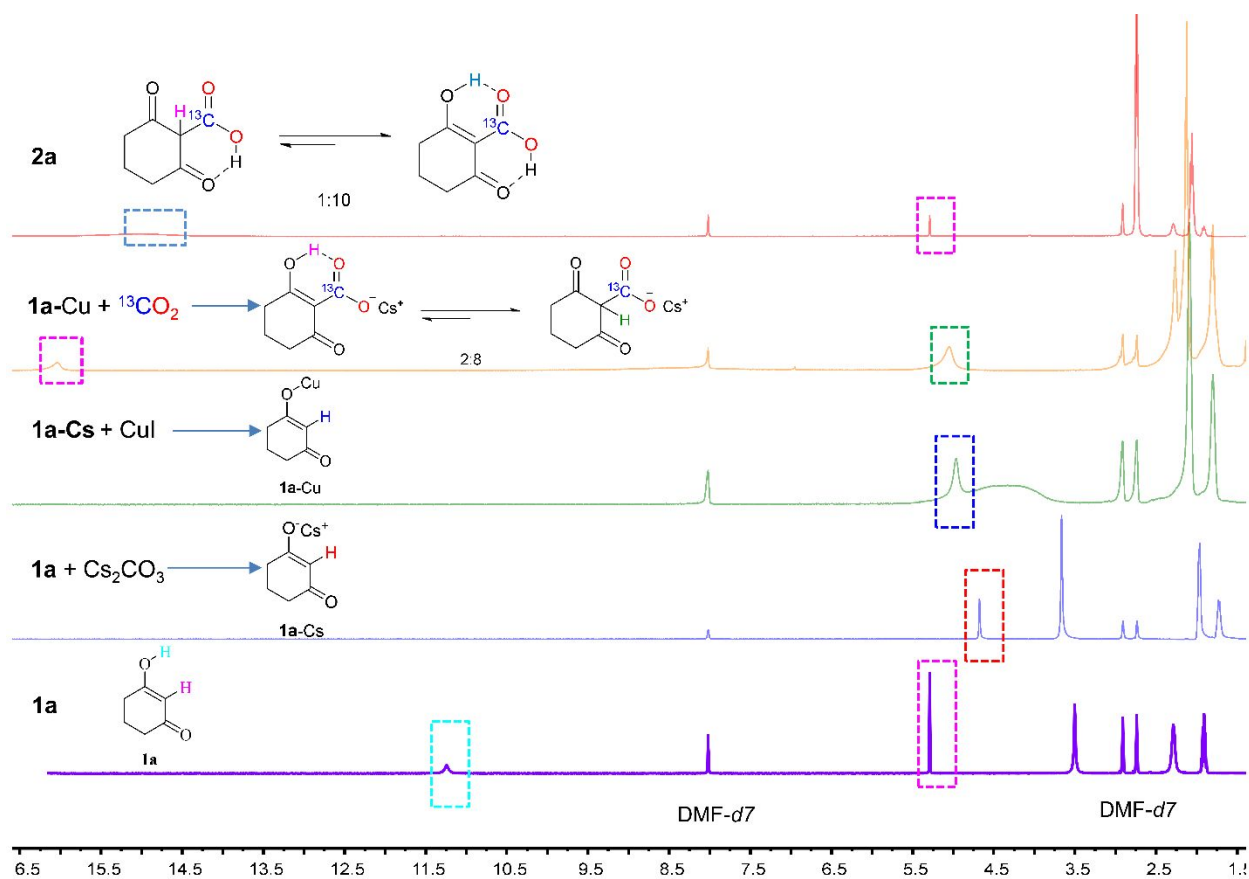
liquid is dried, grind it into 24 holes, and insert 3 instar larvae into each hole, each time using 10 heads. Three repetitions, a total of 30 test worms, mainly stomach poisoning, contact toxicity, while observing the larva feeding phenomenon. The mortality rate was checked after 72 h.

#### ***Ostrinia nubilalis hubner* killing activity test**

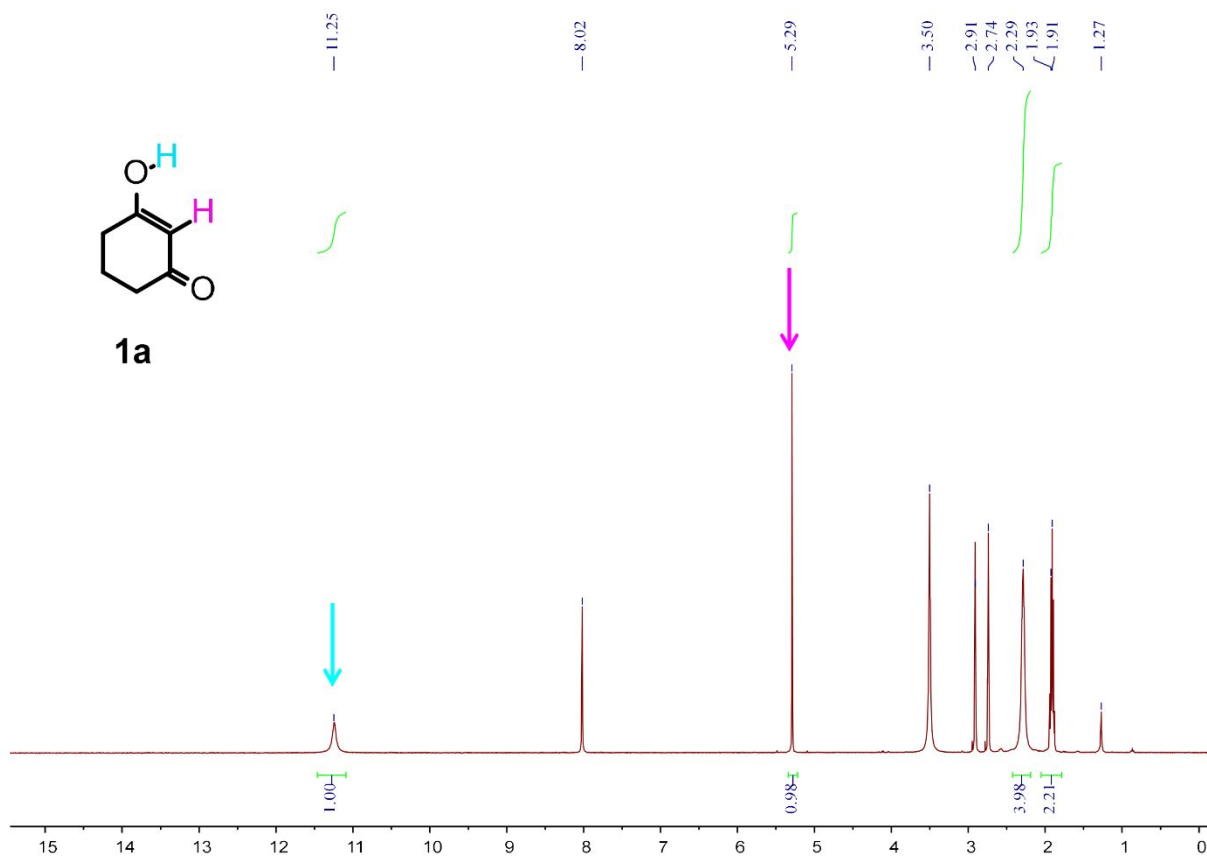
*Ostrinia nubilalis hubner*, a normal population raised indoors. Test method: leaf dipping method. Leaf dipping method, using corn leaf soaked in acetone solution (600 ppm, 600 mg/L). After the liquid is dry, 10 heads of 3rd instar larvae are inserted into the petri dish, and three replicates are performed. For stomach poisoning, contact toxicity, while observing larva feeding phenomenon. The mortality rate was checked after 72 h.



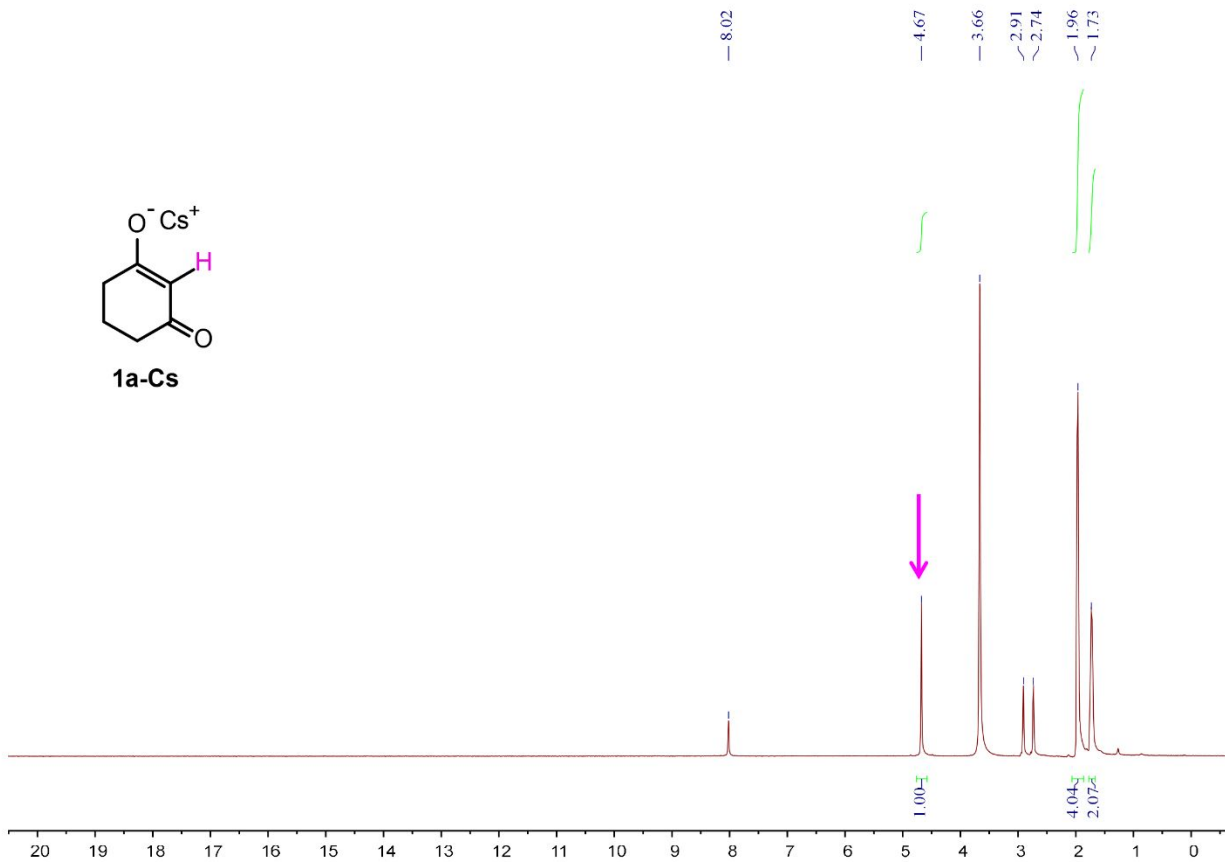
**Figure S1.** A summary of organic chemicals produced from  $\text{CO}_2$  utilization.



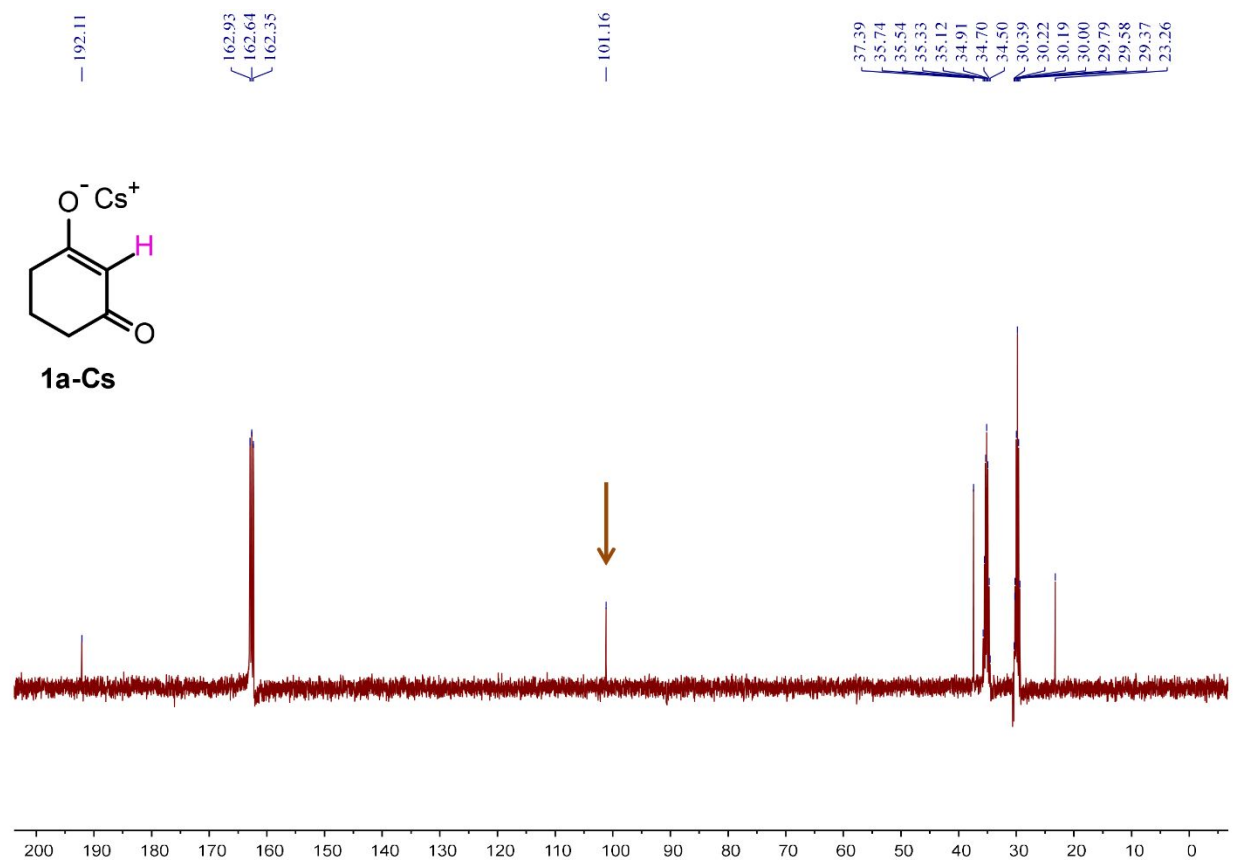
**Figure S2.** The step-by-step tracking of the reaction of CO<sub>2</sub> with **1a** through <sup>1</sup>H NMR (dmf-d<sub>7</sub> as solvent). The slash boxes in different colours assign the peak positions of corresponding hydrogen atoms, respectively. The ratios of enol and ketone in the solvent are given by the integrations of corresponding peaks.



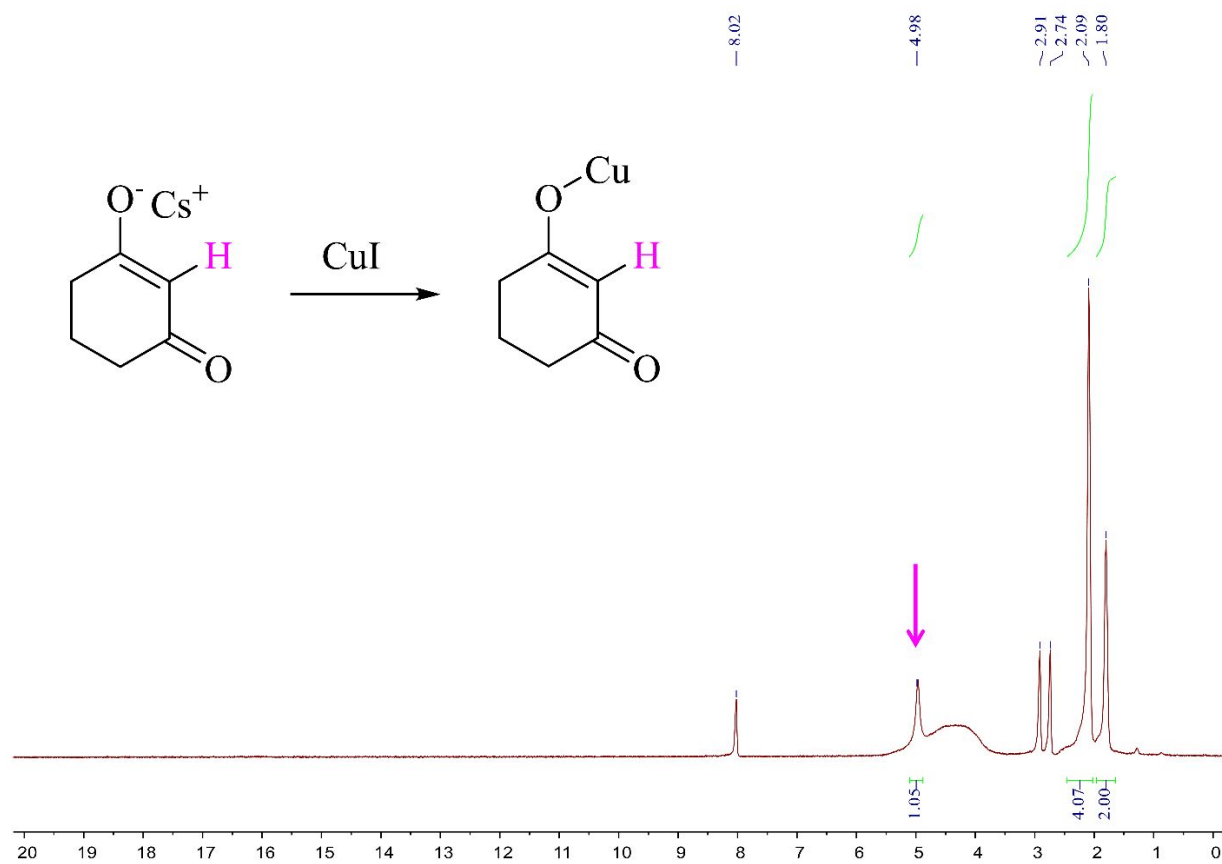
**Figure S3.**  $^1\text{H}$  NMR spectrum of **1a** in  $\text{dmf-}d_7$ .



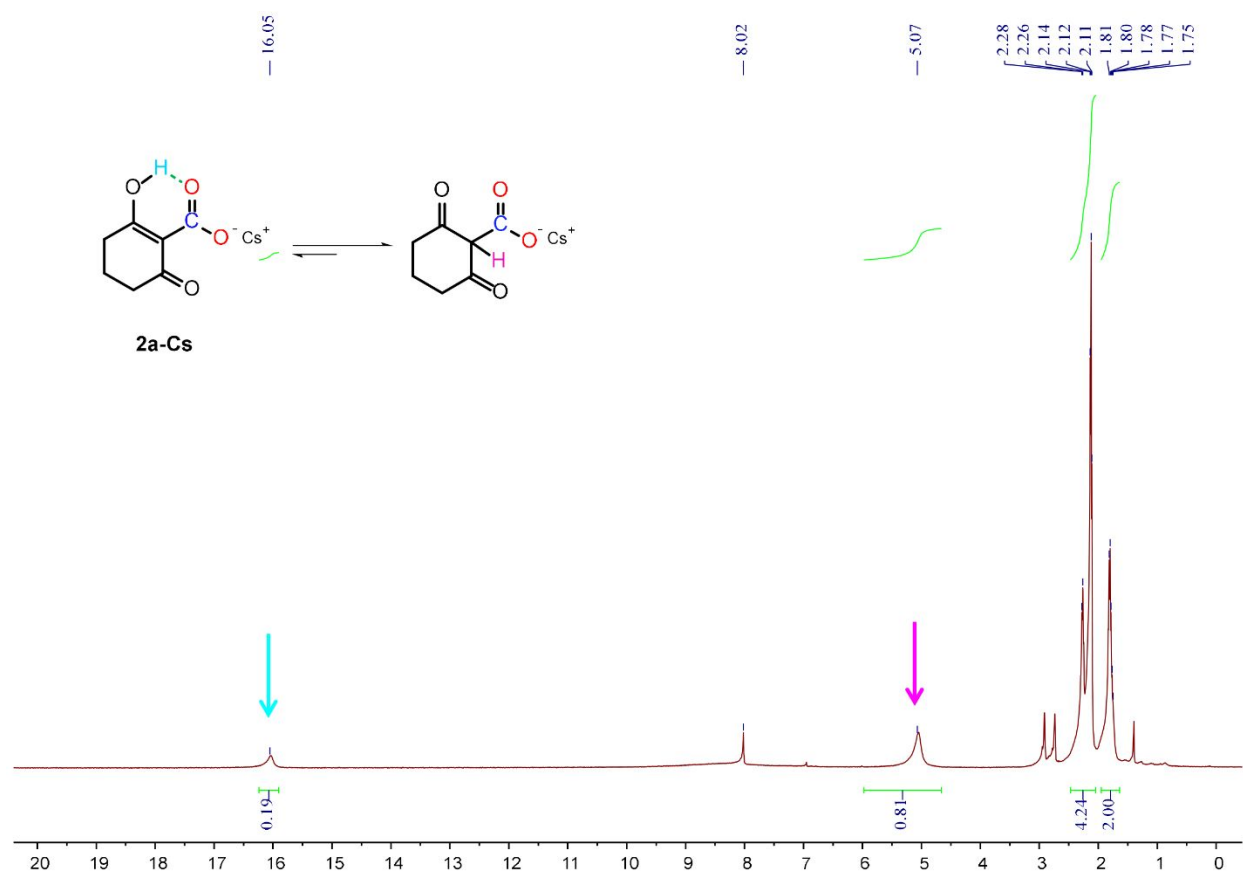
**Figure S4.**  $^1\text{H}$  NMR spectrum of (**1a** +  $\text{Cs}_2\text{CO}_3$ ) in  $\text{dmf-}d_7$ .



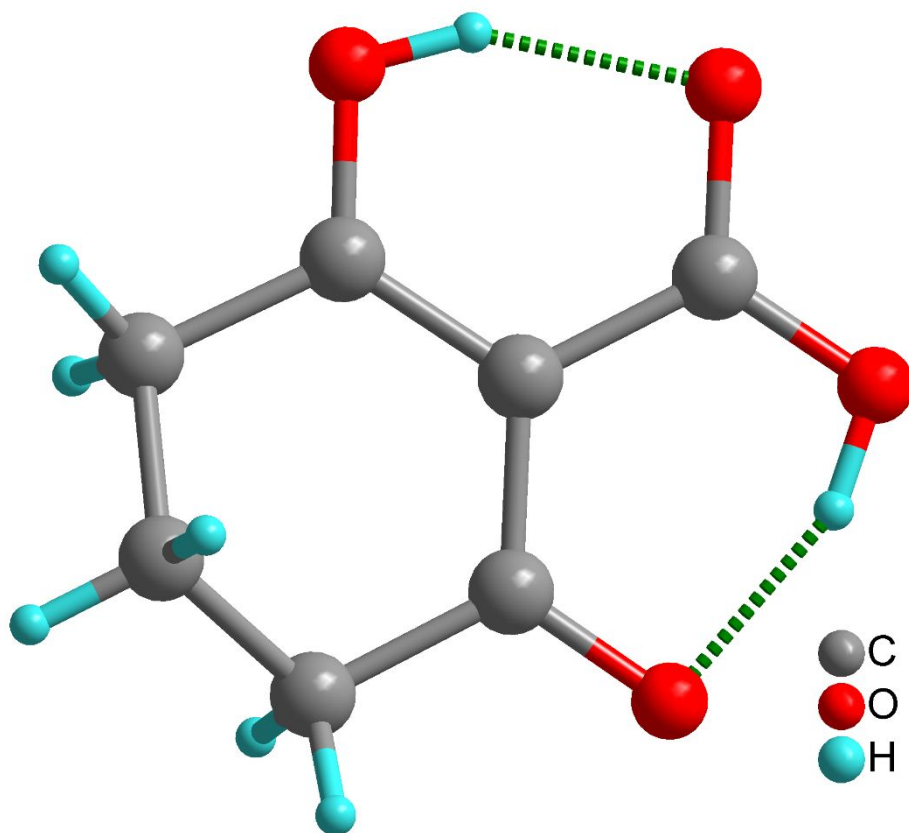
**Figure S5.**  $^{13}\text{C}$  NMR spectrum of (**1a** +  $\text{Cs}_2\text{CO}_3$ ) in dmf- $d_7$ .



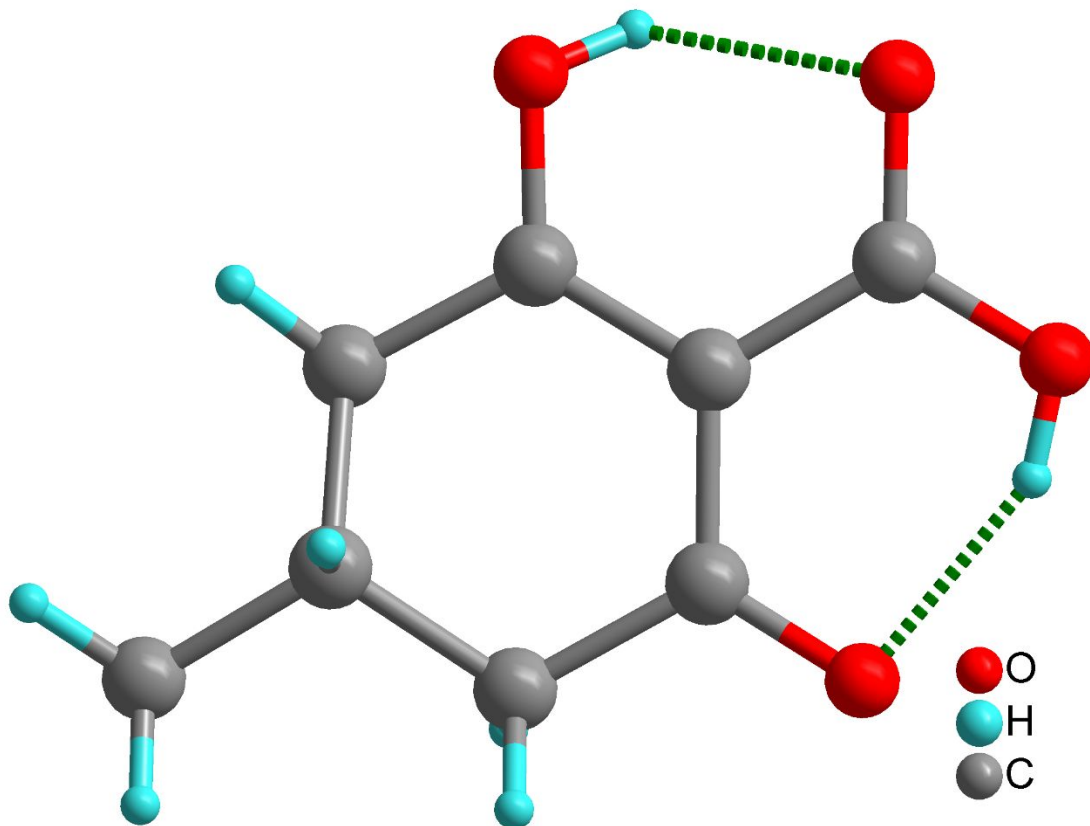
**Figure S6.** <sup>1</sup>H NMR spectrum of (**1a** + Cs<sub>2</sub>CO<sub>3</sub> + CuI) with dmf-*d*<sub>7</sub> as solvent.



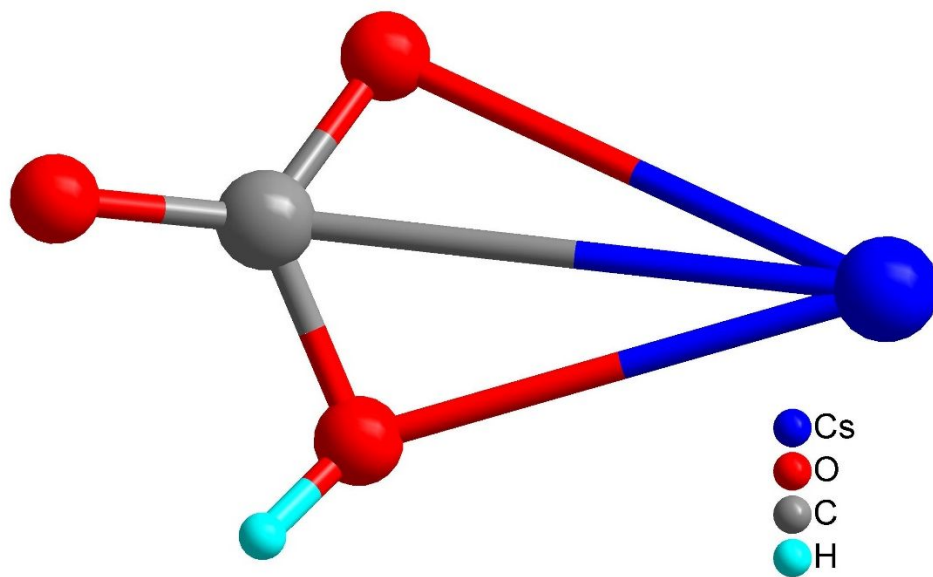
**Figure S7.**  $^1\text{H}$  NMR spectrum of **1a** after reaction 24 h in dmf- $d_7$ .



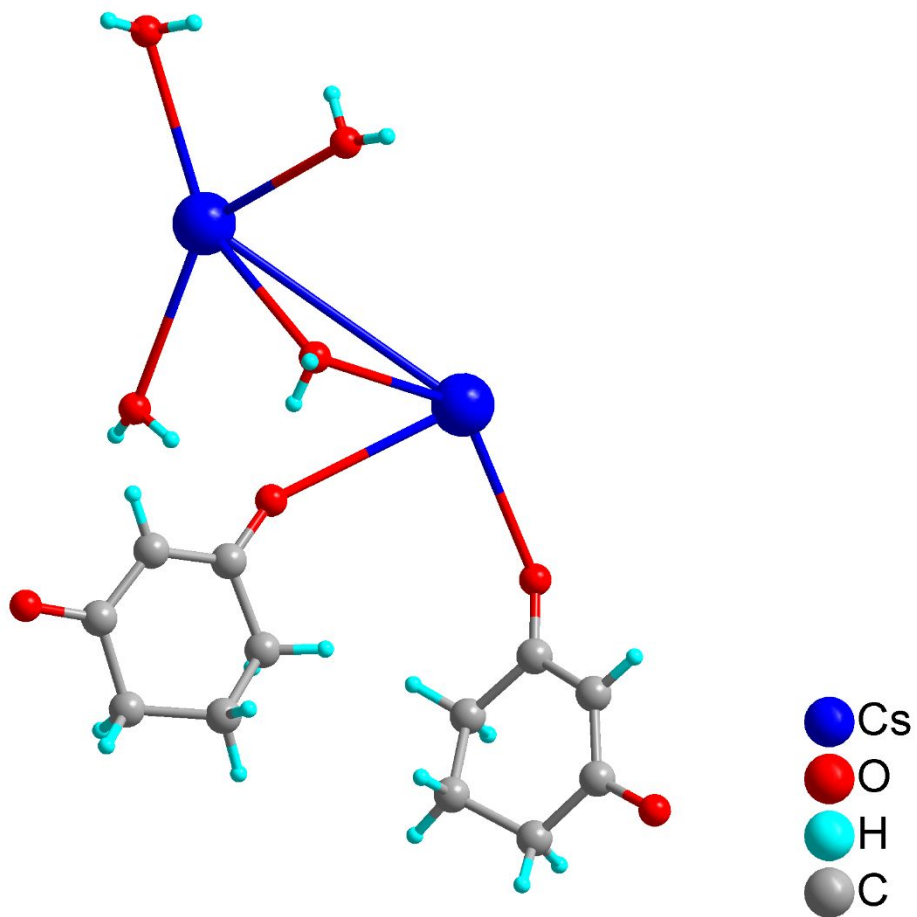
**Figure S8.** A ball-and-stick diagram of **2a**.



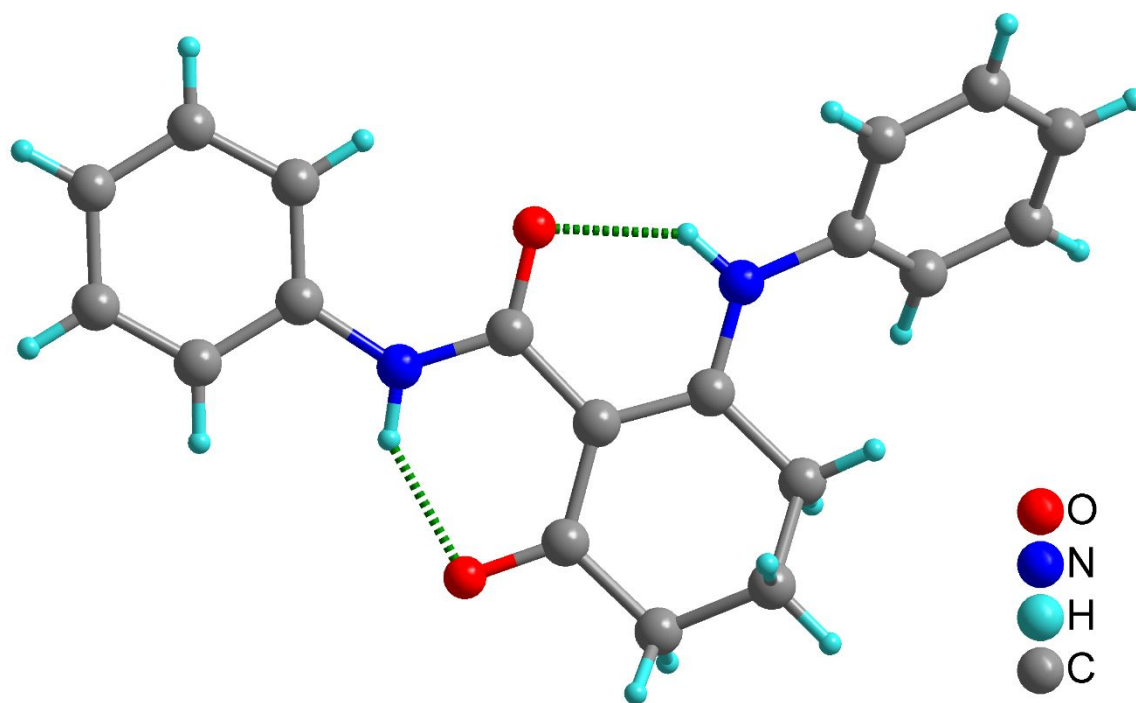
**Figure S9.** A ball-and-stick diagram of **2b**.



**Figure S10.** A ball-and-stick diagram of  $\text{CsHCO}_3$ .

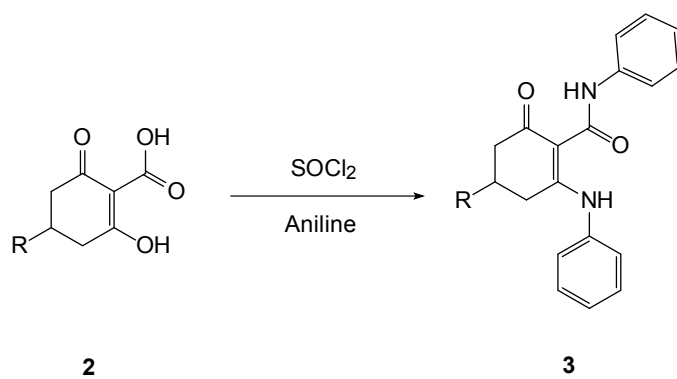


**Figure S11.** A ball-and-stick diagram of  $C_{24}H_{42}Cs_4O_{15}$  (**1a-Cs**).



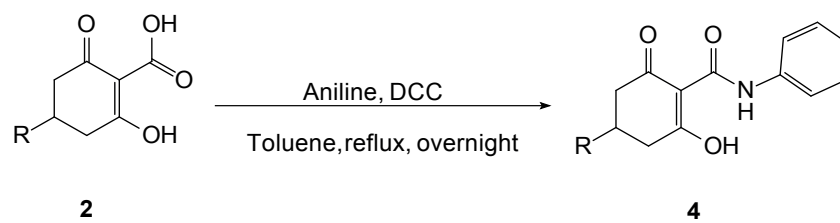
**Figure S12.** A ball-and-stick diagram of **3a**.

**Table S1.** Isolated Yield of **3a-3e**.



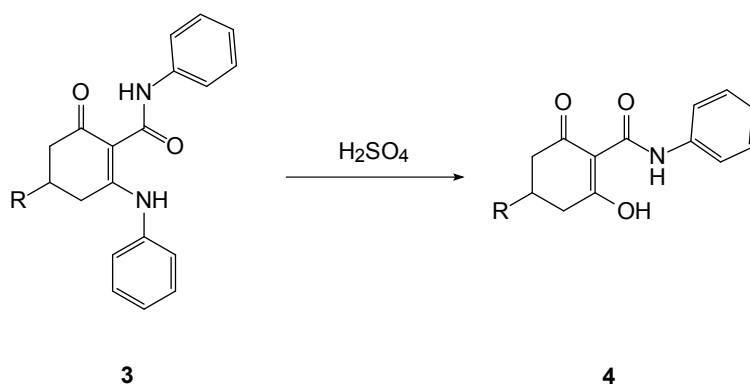
	Isolated Yield
<b>3a</b>	78%
<b>3b</b>	81%
<b>3c</b>	77%
<b>3d</b>	83%
<b>3e</b>	80%

**Table S2.** Isolated Yield of **4a-4e** from **2**.



	Isolated Yield
<b>4a</b>	55%
<b>4b</b>	64%
<b>4c</b>	51%
<b>4d</b>	56%
<b>4e</b>	53%

**Table S3.** Isolated Yield of **4a-4e** from **3**.



	Isolated Yield
<b>4a</b>	90%
<b>4b</b>	88%
<b>4c</b>	89%
<b>4d</b>	91%
<b>4e</b>	86%

**Table S4.** Insecticidal Activity of Compound **3a-3e**.

Insecticide	<i>Mythimna separata walker</i>		<i>Culex pipiens pallens</i>	
	Concentration	Mortality	Concentration	Mortality
<b>3a</b>	600(ppm)	100%	10(ppm)	20%
<b>3b</b>	600(ppm)	35%	10(ppm)	70%
<b>3c</b>	600(ppm)	30%	10(ppm)	80%
<b>3d</b>	200(ppm)	100%	10(ppm)	20%
<b>3e</b>	600(ppm)	55%	10(ppm)	100%

Insecticide	<i>Helicoverpa armigera</i>		<i>Ostrinia nubilalis hubner</i>	
	Concentration	Mortality	Concentration	Mortality
<b>3a</b>	600(ppm)	75%	600(ppm)	70%
<b>3b</b>	600(ppm)	15%	600(ppm)	20%
<b>3c</b>	600(ppm)	10%	600(ppm)	15%
<b>3d</b>	600(ppm)	100%	600(ppm)	100%
<b>3e</b>	600(ppm)	25%	600(ppm)	30%

**Table S5.** Crystallographic data and structure refinements.

	<b>2a</b>	<b>2b</b>	<b>3a</b>	<b>C<sub>24</sub>H<sub>42</sub>Cs<sub>4</sub>O<sub>15</sub></b>	<b>CsHCO<sub>3</sub></b>
Formula	C <sub>7</sub> H <sub>8</sub> O <sub>4</sub>	C <sub>8</sub> H <sub>10</sub> O <sub>4</sub>	C <sub>19</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub>	C <sub>24</sub> H <sub>42</sub> Cs <sub>4</sub> O <sub>15</sub>	CsHCO <sub>3</sub>
Mol. wt.	156.13	170.16	306.35	1102.21	193.93
Crystal system	Monoclinic	Monoclinic	Monoclinic	orthorhombic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> (Å)	7.3799(2)	5.4266(2)	18.7761(10)	16.3847(15)	4.59793(19)
<i>b</i> (Å)	10.2055(3)	13.3919(5)	12.1408(6)	23.6354(17)	11.2050(4)
<i>c</i> (Å)	9.6550(3)	11.0530(5)	14.3438(8)	4.6617(4)	7.1030(3)
<i>α</i> (deg)	90	90	90	90	90
<i>β</i> (deg)	111.852(4)	102.437(4)	106.851(6)	90	102.035(4)
<i>γ</i> (deg)	90	90	90	90	90
<i>V</i> (Å <sup>3</sup> )	674.93(4)	784.40(6)	3129.4(3)	1805.3(3)	357.90(2)
<i>Z</i>	4	4	8	2	4
<i>T</i> (K)	120(10)	120(10)	120(10)	150(10)	120(10)
<i>ρ</i> calcd. (Mg/m <sup>3</sup> )	1.537	1.441	1.300	2.028	3.599
<i>μ</i> (mm <sup>-1</sup> )	0.128	0.116	0.085	4.067	10.159
Reflns collected	4436	4623	17326	3985	1916
Reflns unique	1190	1387	5409	2637	625
	( <i>R</i> <sub>int</sub> = 0.0185)	( <i>R</i> <sub>int</sub> = 0.0222)	( <i>R</i> <sub>int</sub> = 0.0902)	( <i>R</i> <sub>int</sub> = 0.0472)	( <i>R</i> <sub>int</sub> = 0.0451)
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0335 <i>wR</i> <sub>2</sub> = 0.0938	<i>R</i> <sub>1</sub> = 0.0510 <i>wR</i> <sub>2</sub> = 0.1410	<i>R</i> <sub>1</sub> = 0.1583 <i>wR</i> <sub>2</sub> = 0.1303	<i>R</i> <sub>1</sub> = 0.0480 <i>wR</i> <sub>2</sub> = 0.0927	<i>R</i> <sub>1</sub> = 0.0308 <i>wR</i> <sub>2</sub> = 0.0842
<i>S</i>	1.060	1.079	1.017	1.018	1.109
Δ <i>ρ</i> max (eÅ <sup>-3</sup> )	0.27	0.73	0.23	1.09	1.96
Δ <i>ρ</i> min (eÅ <sup>-3</sup> )	-0.22	-0.46	-0.27	-0.75	-1.04
CCDC	1955775	1955776	1980055	1955777	1955778

## NMR data for all products

**1,3-Cyclohexanedione-2-acid (2a).** Pale yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.87 (s, 1H), 2.62 (s, 4H), 2.02 (s, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  198.07, 198.07, 173.60, 102.65, 32.86, 32.86, 18.79; HRMS(ESI): Calcd for  $\text{C}_7\text{H}_8\text{O}_4$   $[\text{M}+\text{H}]^+$ : 156.0423, found 157.0494.

**5-methyl-1,3-Cyclohexanedione-2-acid (2b).** Pale yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.81 (s, 1H), 1.99-2.63 (m, 5H), 1.08 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  197.78, 197.78, 173.64, 102.49, 41.01, 26.74, 26.74, 20.63; HRMS(ESI): Calcd for  $\text{C}_8\text{H}_{10}\text{O}_4$   $[\text{M}-\text{H}]^-$ : 170.0579, found 169.0506.

**5,5-dimethyl-1,3-Cyclohexanedione-2-acid (2c).** Yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.79 (s, 1H), 2.51 (s, 4H), 1.12 (s, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  197.17, 197.17, 173.53, 101.80, 46.70, 46.70, 31.48, 28.22, 28.22; HRMS(ESI): Calcd for  $\text{C}_9\text{H}_{12}\text{O}_4$   $[\text{M}+\text{H}]^+$ : 184.0736, found 185.0809.

**5-ethyl-1,3-Cyclohexanedione-2-acid (2d).** Yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.81 (s, 1H), 2.68-2.72 (d,  $J = 8$  Hz, 2H), 2.34 (s, 2H), 2.06 (s, 1H), 1.45 (s, 2H), 0.94 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  197.74, 197.74, 173.48, 102.50, 38.95, 33.17, 33.17, 27.97, 10.79; HRMS(ESI): Calcd for  $\text{C}_9\text{H}_{12}\text{O}_4$   $[\text{M}+\text{H}]^+$ : 184.0736, found 185.0804.

**5-propyl-1,3-Cyclohexanedione-2-acid (2e).** Yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.84 (s, 1H), 2.04-2.74 (m, 5H), 1.39 (s, 4H), 0.90-0.94 (t,  $J = 8$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  197.83, 197.83, 173.62, 102.72, 39.44, 37.45, 31.49, 19.60, 19.60, 14.04; HRMS(ESI): Calcd for  $\text{C}_{10}\text{H}_{14}\text{O}_4$   $[\text{M}+\text{H}]^+$ : 198.0892, found 199.0968.

**6-oxo-N-phenyl-2-(phenylamino)cyclohex-1-ene-1-carboxamide (3a).** White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.11 (s, 1H), 12.51 (s, 1H), 7.61-7.63 (d,  $J = 8$  Hz, 2H), 7.39-

7.43 (t,  $J = 8$  Hz, 2H), 7.31-7.34 (t,  $J = 8$  Hz, 3H), 7.16-7.18 (d,  $J = 8$  Hz, 2H), 7.06-7.09 (t,  $J = 8$  Hz, 1H), 2.54-2.62 (m, 4H), 1.87-1.89 (m, 2H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.32, 172.70, 168.78, 138.60, 137.31, 129.50, 129.50, 128.87, 128.87, 127.35, 125.85, 125.85, 123.72, 121.18, 121.18, 100.29, 38.15, 28.94, 20.40 ppm; HRMS(ESI): calcd for  $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2$   $[\text{M}+\text{H}]^+$ : 306.1368, found 307.1446.

**4-methyl-6-oxo-N-phenyl-2-(phenylamino)cyclohex-1-ene-1-carboxamide (3b).** White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.11 (s, 1H), 12.52 (s, 1H), 7.62-7.64 (d,  $J = 8$  Hz, 2H), 7.40-7.44 (t,  $J = 8$  Hz, 2H), 7.30-7.34 (m, 3H), 7.16-7.18 (d,  $J = 8$  Hz, 2H), 7.06-7.09 (t,  $J = 8$  Hz, 1H), 2.56-2.70 (m, 2H), 2.20-2.31 (m, 2H), 2.09-2.12 (m, 1H), 0.99-1.01 (d,  $J = 8$  Hz, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.20, 172.18, 168.67, 138.61, 137.29, 129.52, 129.52, 128.86, 128.86, 127.33, 125.82, 125.82, 123.69, 121.13, 121.13, 99.95, 46.22, 36.67, 27.61, 20.89 ppm; HRMS(ESI): calcd for  $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_2$   $[\text{M}+\text{H}]^+$ : 320.1525, found 321.1596.

**4,4-dimethyl-6-oxo-N-phenyl-2-(phenylamino)cyclohex-1-ene-1-carboxamide (3c).** White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.14 (s, 1H), 12.50 (s, 1H), 7.62-7.64 (d,  $J = 8$  Hz, 2H), 7.40-7.44 (t,  $J = 8$  Hz, 2H), 7.30-7.34 (t,  $J = 8$  Hz, 3H), 7.15-7.17 (d,  $J = 8$  Hz, 2H), 7.06-7.09 (t,  $J = 8$  Hz, 1H), 2.40-2.47 (m, 4H), 1.03 (m, 2H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  195.70, 171.50, 168.68, 138.65, 137.35, 129.59, 129.59, 128.88, 128.88, 127.44, 126.03, 126.03, 123.71, 121.12, 121.12, 99.34, 51.65, 41.88, 31.19, 27.98, 27.98 ppm; HRMS(ESI): calcd for  $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_2$   $[\text{M}+\text{H}]^+$ : 334.1681, found 335.1752.

**4-ethyl-6-oxo-N-phenyl-2-(phenylamino)cyclohex-1-ene-1-carboxamide (3d).** White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.10 (s, 1H), 12.49 (s, 1H), 7.60-7.62 (d,  $J = 8$  Hz, 2H), 7.41-7.44 (t,  $J = 8$  Hz, 2H), 7.30-7.34 (t,  $J = 8$  Hz, 3H), 7.16-7.18 (d,  $J = 8$  Hz, 2H),

7.06-7.10 (t,  $J = 8$  Hz, 1H), 2.64-2.73 (m, 2H), 2.19-2.33 (m, 2H), 1.87-1.93 (m, 1H), 1.32-1.40 (m, 2H), 0.84-0.88 (t,  $J = 8$  Hz, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.31, 172.29, 168.73, 138.65, 137.38, 129.59, 129.59, 128.92, 128.92, 127.41, 125.89, 125.89, 123.78, 121.25, 121.25, 100.18, 44.04, 34.85, 34.07, 28.20, 11.03 ppm; HRMS(ESI): calcd for  $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_2$   $[\text{M}+\text{H}]^+$ : 334.1681, found 335.1758.

**6-oxo-N-phenyl-2-(phenylamino)-4-propylcyclohex-1-ene-1-carboxamide (3e).** White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.09 (s, 1H), 12.49 (s, 1H), 7.61-7.63 (d,  $J = 8$  Hz, 2H), 7.40-7.44 (t,  $J = 8$  Hz, 2H), 7.30-7.34 (t,  $J = 8$  Hz, 3H), 7.16-7.18 (d,  $J = 8$  Hz, 2H), 7.06-7.09 (t,  $J = 8$  Hz, 1H), 2.62-2.71 (m, 2H), 2.19-2.32 (m, 2H), 1.96-2.04 (m, 1H), 1.27-1.30 (m, 4H), 0.84-0.87 (t,  $J = 8$  Hz, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.26, 172.24, 168.69, 138.64, 137.34, 129.56, 129.56, 128.89, 128.89, 127.36, 125.84, 125.84, 123.74, 121.20, 121.20, 100.15, 44.35, 37.58, 35.16, 32.20, 19.63, 14.10 ppm; HRMS(ESI): calcd for  $\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_2$   $[\text{M}+\text{H}]^+$ : 348.1838, found 349.1912.

**2-hydroxy-6-oxo-N-phenylcyclohex-1-ene-1-carboxamide (4a).** White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  17.94 (s, 1H), 11.84 (s, 1H), 7.55-7.57 (d,  $J = 8$  Hz, 2H), 7.33-7.37 (t,  $J = 8$  Hz, 2H), 7.14-7.18 (t,  $J = 8$  Hz, 1H), 2.66-2.69 (t,  $J = 8$  Hz, 2H), 2.54-2.57 (t,  $J = 8$  Hz, 2H), 1.99-2.04 (m, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  197.97, 195.81, 169.80, 136.74, 129.17, 129.17, 125.23, 121.60, 121.60, 100.11, 37.67, 32.26, 19.44; HRMS(ESI): Calcd for  $\text{C}_{13}\text{H}_{13}\text{NO}_3$   $[\text{M}+\text{H}]^+$ : 231.0895, found 232.0972.

**2-hydroxy-4-methyl-6-oxo-N-phenylcyclohex-1-ene-1-carboxamide (4b).** White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  17.87 (s, 1H), 11.81 (s, 1H), 7.55-7.57 (d,  $J = 8$  Hz, 2H), 7.33-7.37 (t,  $J = 8$  Hz, 2H), 7.14-7.18 (t,  $J = 8$  Hz, 1H), 2.58-2.71 (m, 2H), 2.24-2.43 (m, 3H), 1.11-1.12 (d,  $J = 4$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  197.83, 195.23, 169.65,

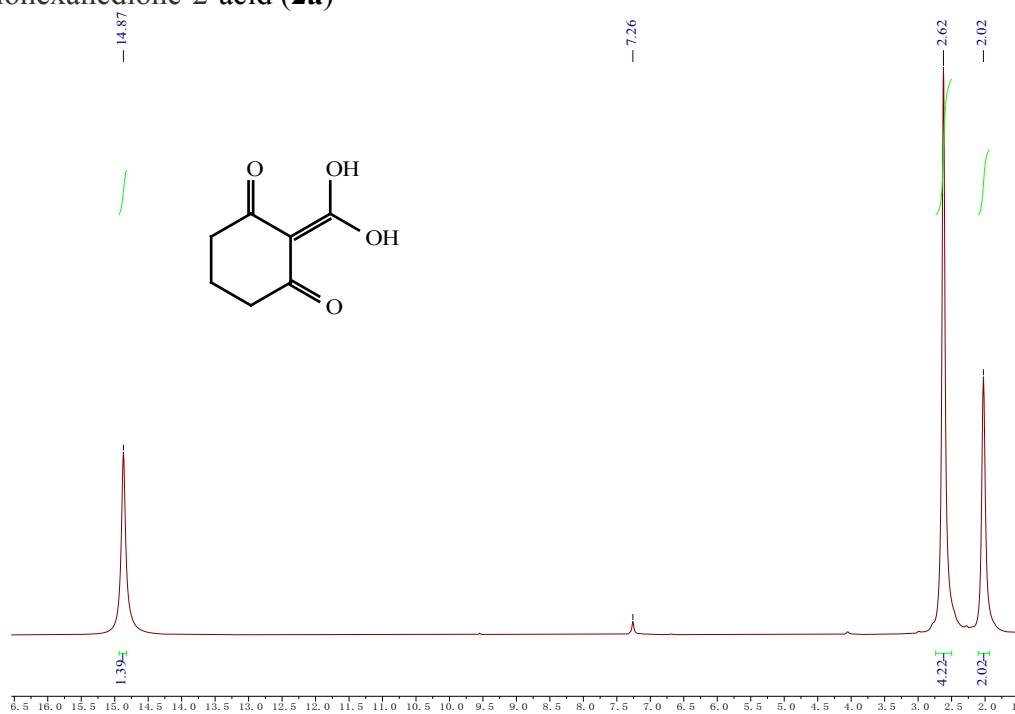
136.74, 129.17, 129.17, 125.21, 121.55, 121.55, 103.04, 45.83, 40.15, 26.99, 20.95; HRMS(ESI): Calcd for C<sub>14</sub>H<sub>15</sub>NO<sub>3</sub> [M+H]<sup>+</sup>: 245.1052, found 246.1123.

**2-hydroxy-4,4-dimethyl-6-oxo-N-phenylcyclohex-1-ene-1-carboxamide (4c).** White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 11.77 (s, 1H), 7.55-7.57 (d, *J* = 8 Hz, 2H), 7.34-7.37 (t, *J* = 8 Hz, 2H), 7.14-7.18 (t, *J* = 8 Hz, 1H), 2.54 (s, 2H), 2.42 (s, 2H), 1.12 (s, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 197.58, 194.47, 169.59, 136.76, 129.18, 129.18, 125.21, 121.54, 121.54, 104.78, 51.44, 45.76, 31.13, 28.33, 28.33; HRMS(ESI): Calcd for C<sub>15</sub>H<sub>17</sub>NO<sub>3</sub> [M+H]<sup>+</sup>: 259.1208, found 260.1278.

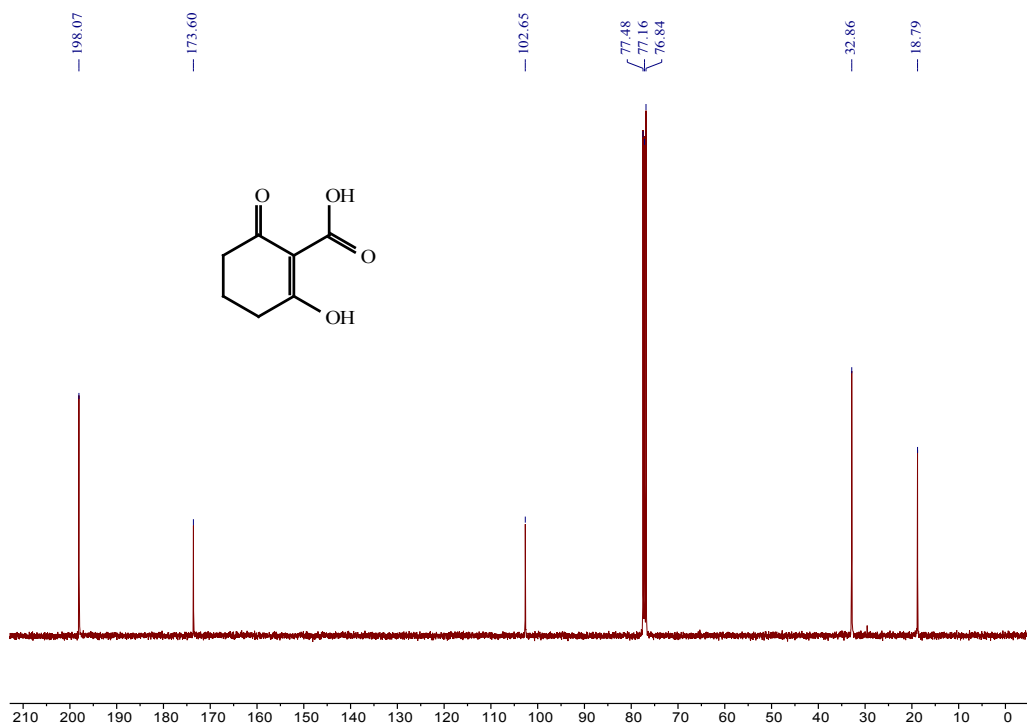
**4-ethyl-2-hydroxy-6-oxo-N-phenylcyclohex-1-ene-1-carboxamide (4d).** White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 17.85 (s, 1H), 11.80 (s, 1H), 7.55-7.57 (d, *J* = 8 Hz, 2H), 7.33-7.37 (t, *J* = 8 Hz, 2H), 7.14-7.17 (t, *J* = 8 Hz, 1H), 2.61-2.74 (m, 2H), 2.21-2.43 (m, 2H), 2.02-2.07 (m, 1H), 1.42-1.49 (m, 2H), 0.95-0.98 (t, *J* = 8 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 197.91, 195.31, 169.61, 136.74, 129.15, 129.15, 125.18, 121.53, 121.53, 103.17, 43.79, 38.13, 33.38, 28.28, 11.04; HRMS(ESI): Calcd for C<sub>15</sub>H<sub>17</sub>NO<sub>3</sub> [M+H]<sup>+</sup>: 259.1208, found 260.1283.

**2-hydroxy-6-oxo-N-phenyl-4-propylcyclohex-1-ene-1-carboxamide (4e).** White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 11.80 (s, 1H), 7.55-7.57 (d, *J* = 8 Hz, 2H), 7.34-7.37 (t, *J* = 8 Hz, 2H), 7.14-7.18 (t, *J* = 8 Hz, 1H), 2.61-2.74 (m, 2H), 2.15-2.43 (m, 3H), 1.38-1.40 (m, 4H), 0.92-0.95 (t, *J* = 8 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 197.91, 195.31, 169.58, 136.71, 129.14, 129.14, 125.17, 121.51, 121.51, 100.07, 44.08, 38.44, 37.61, 31.48, 19.65, 14.11; HRMS(ESI): Calcd for C<sub>16</sub>H<sub>19</sub>NO<sub>3</sub> [M+H]<sup>+</sup>: 273.1365, found 274.1441.

**$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR Spectra**  
1,3-Cyclohexanedione-2-acid (**2a**)

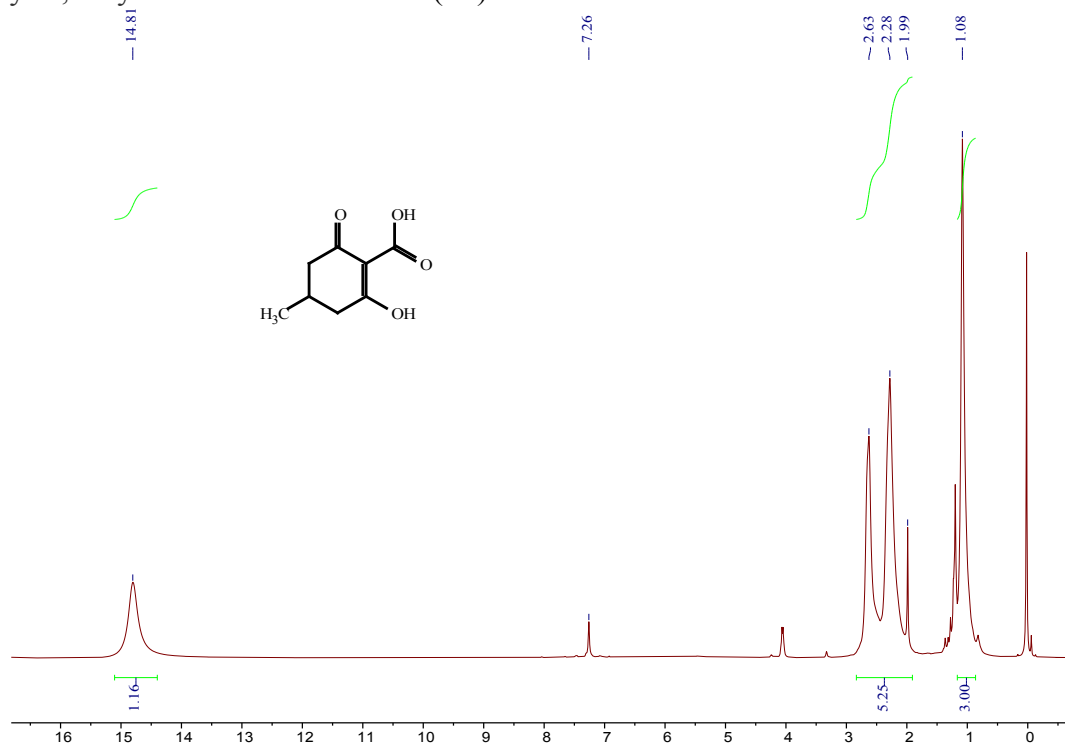


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **2a**.

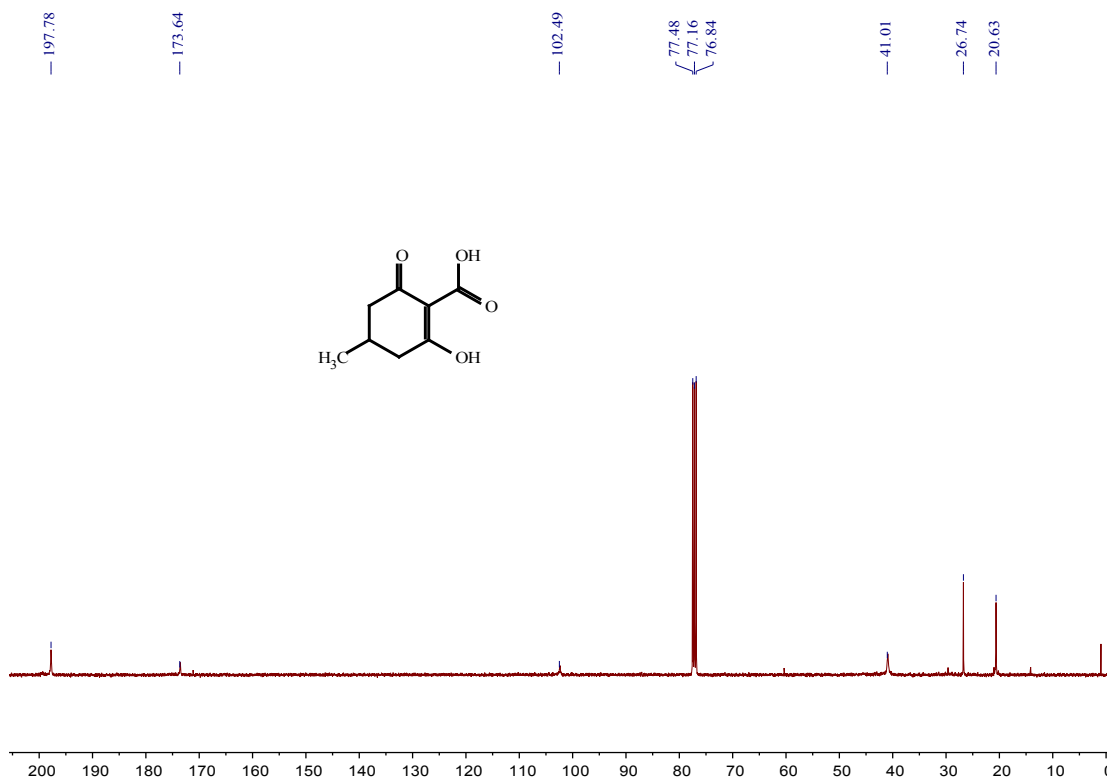


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **2a**.

5-methyl-1,3-Cyclohexanedione-2-acid (**2b**)

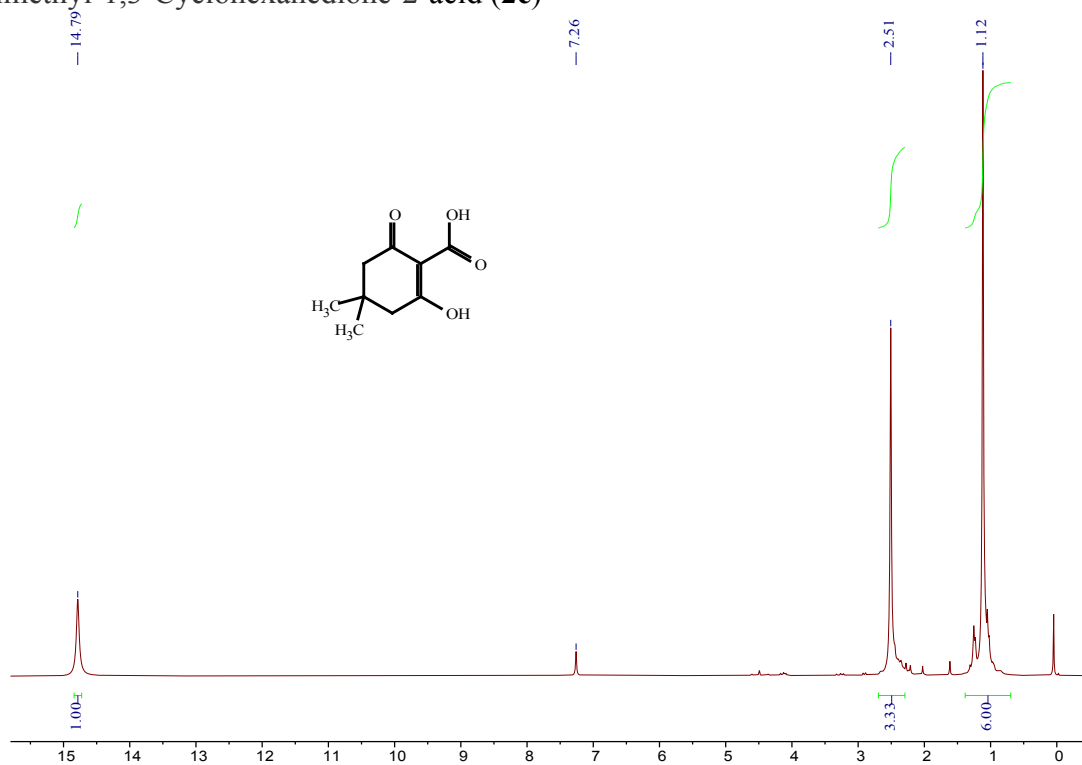


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **2b**.

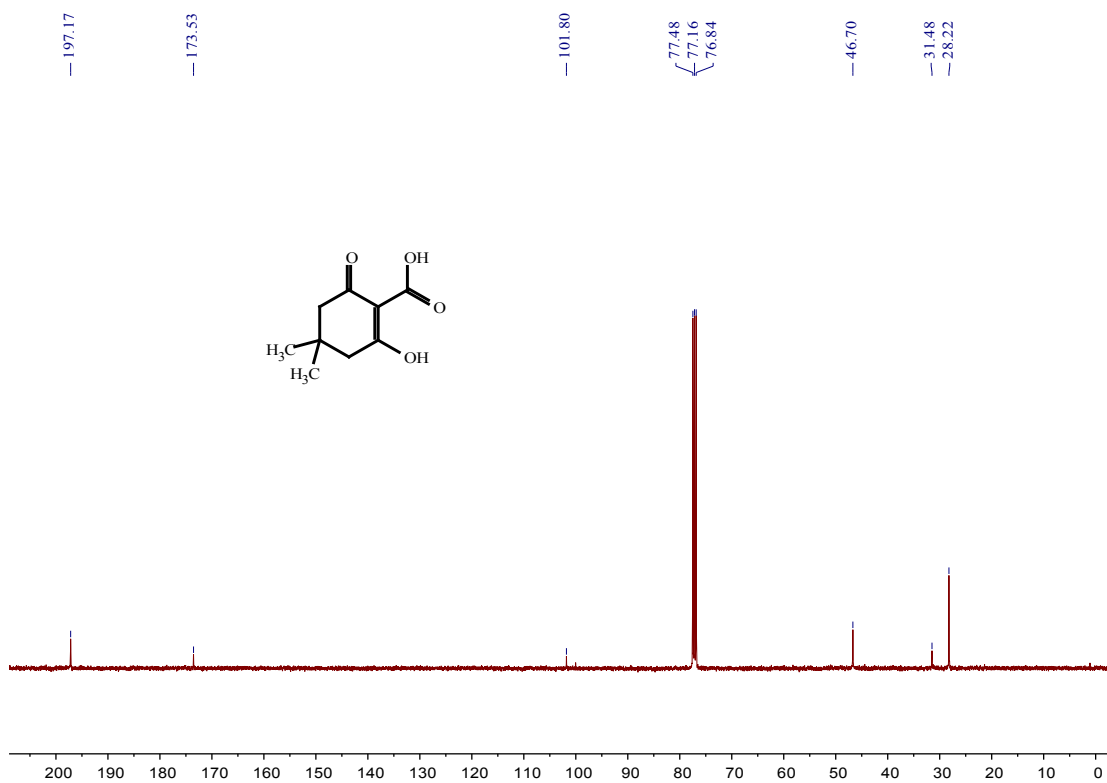


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **2b**.

5,5-dimethyl-1,3-Cyclohexanedione-2-acid (**2c**)

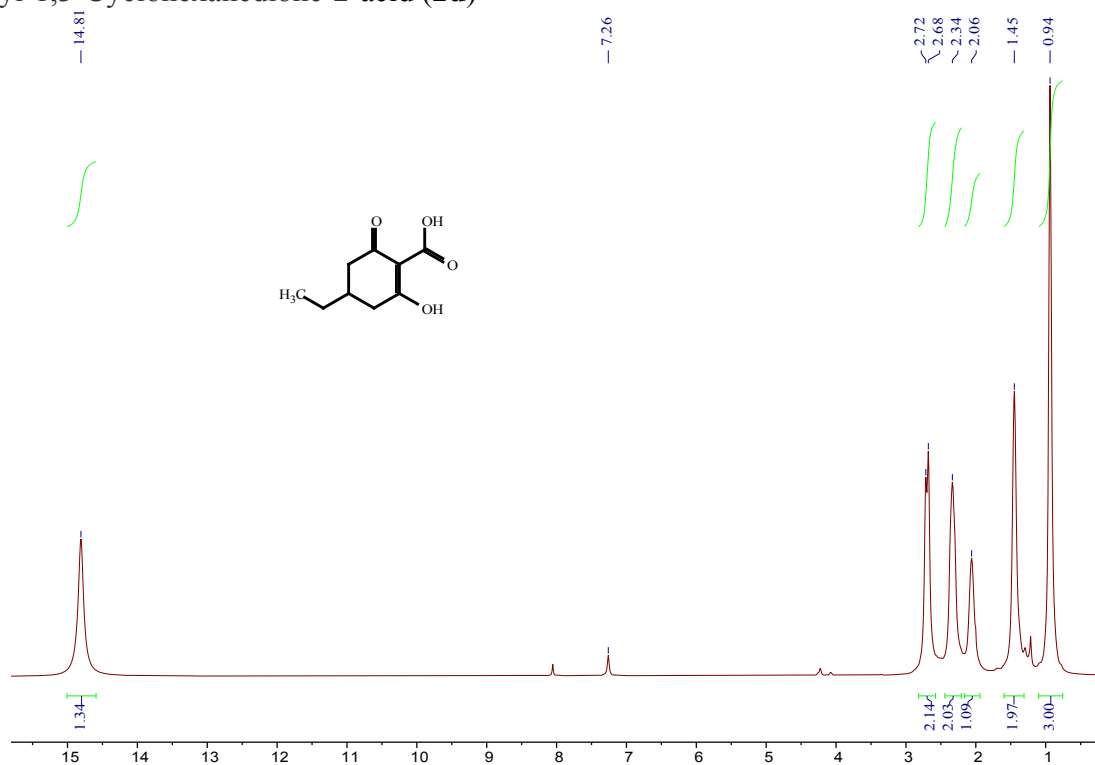


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **2c**.

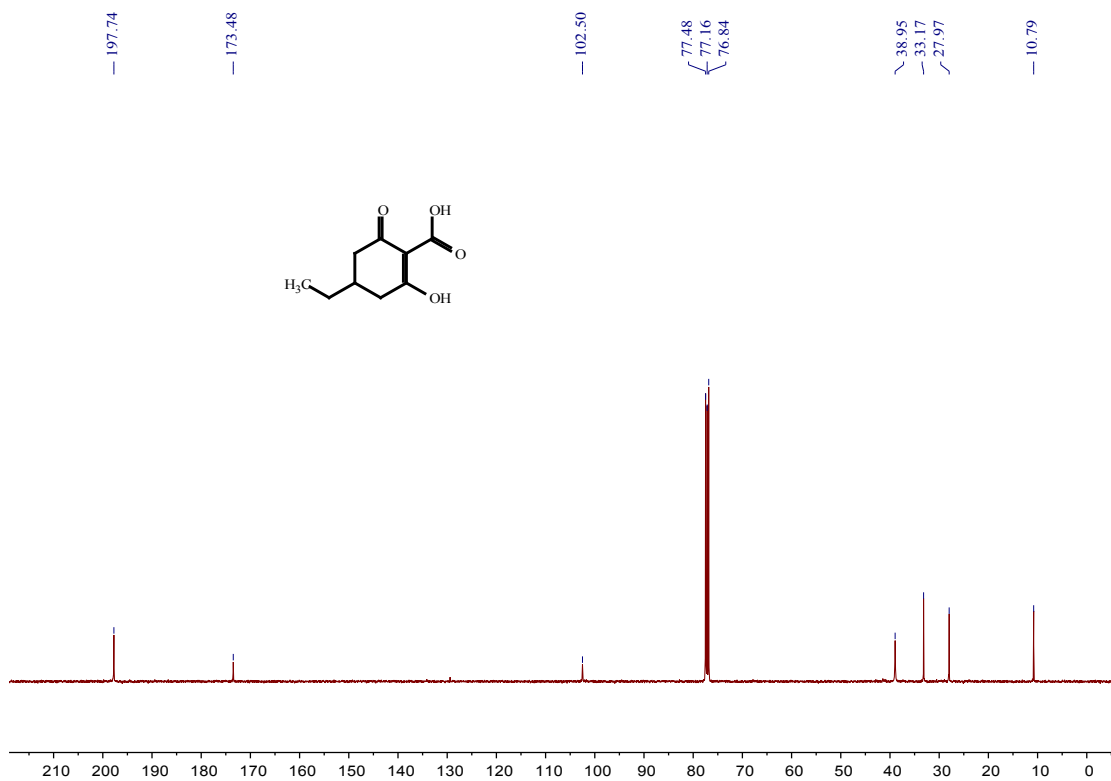


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **2c**.

5-ethyl-1,3-Cyclohexanedione-2-acid (**2d**)

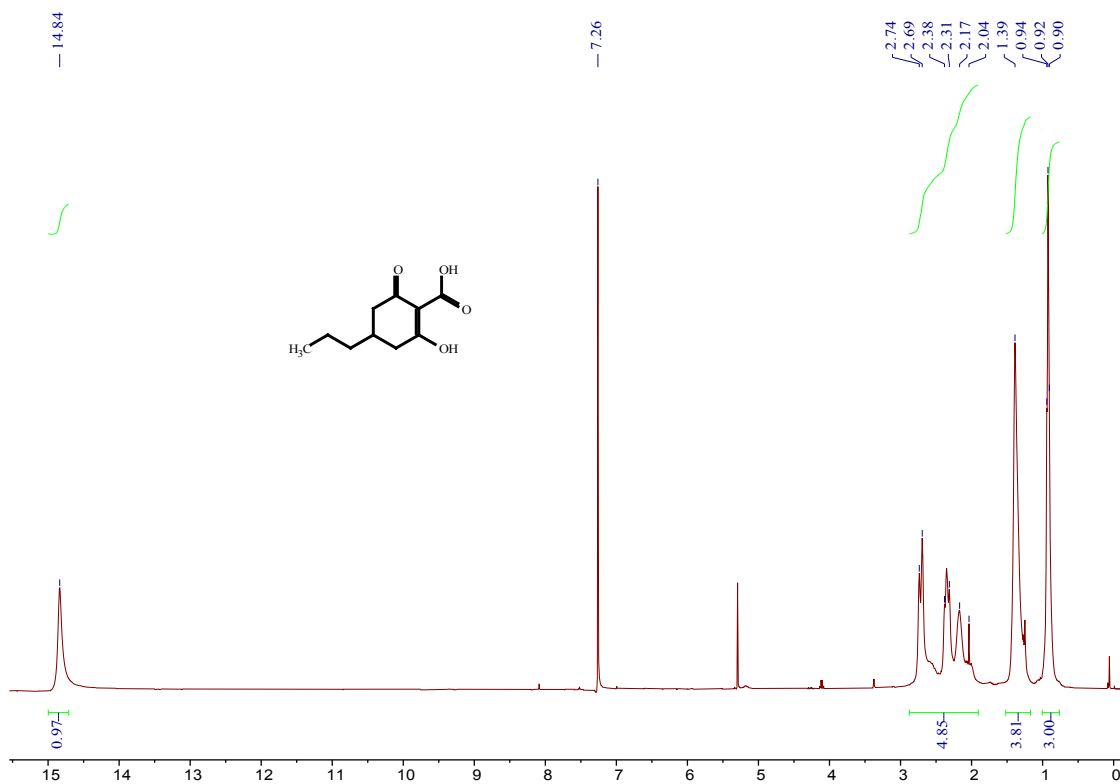


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **2d**.

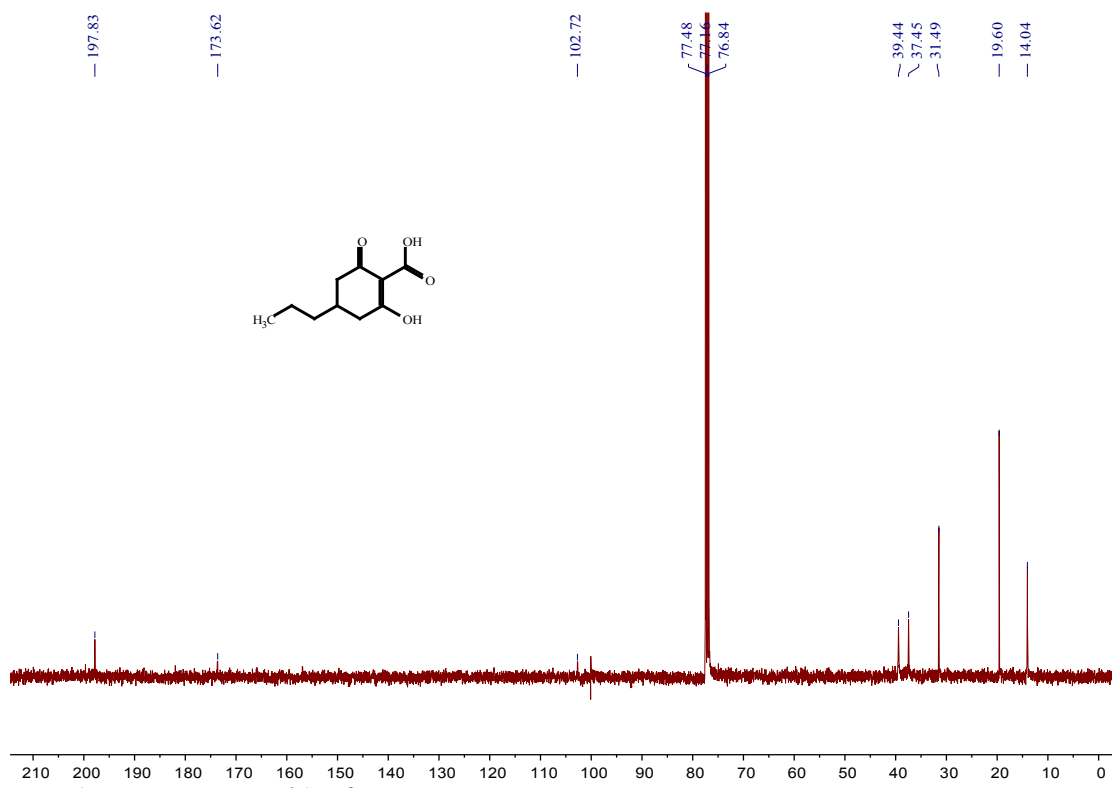


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **2d**.

5-propyl-1,3-Cyclohexanedione-2-acid (**2e**)

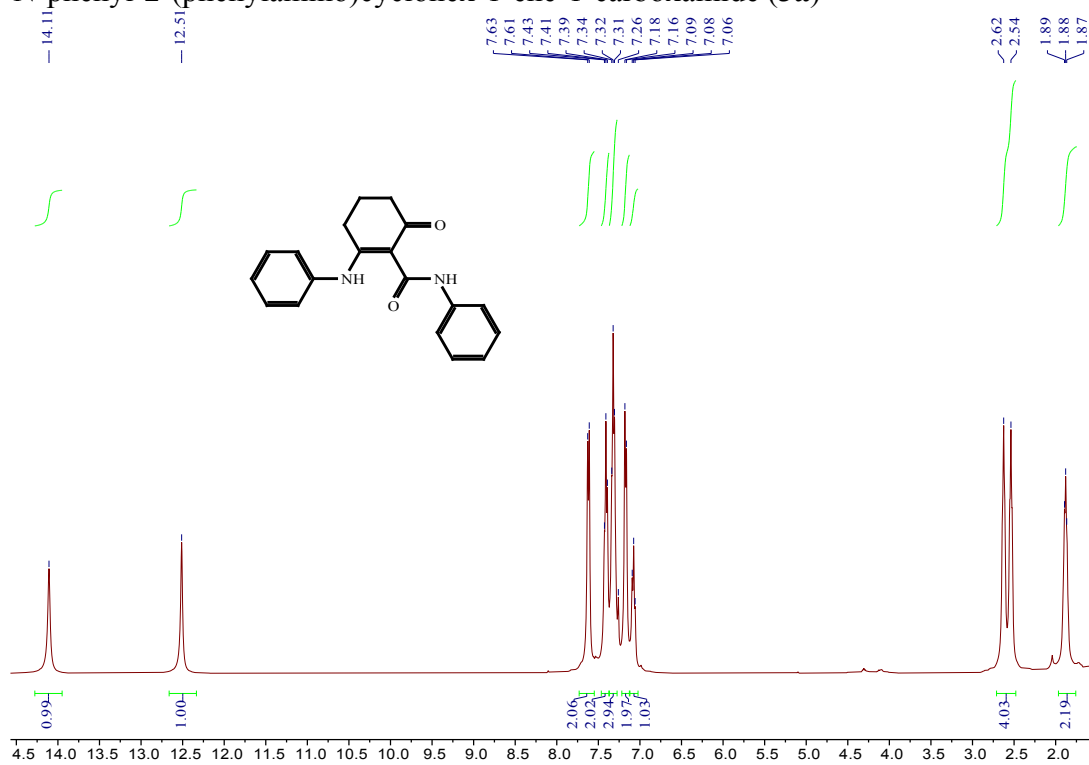


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **2e**.

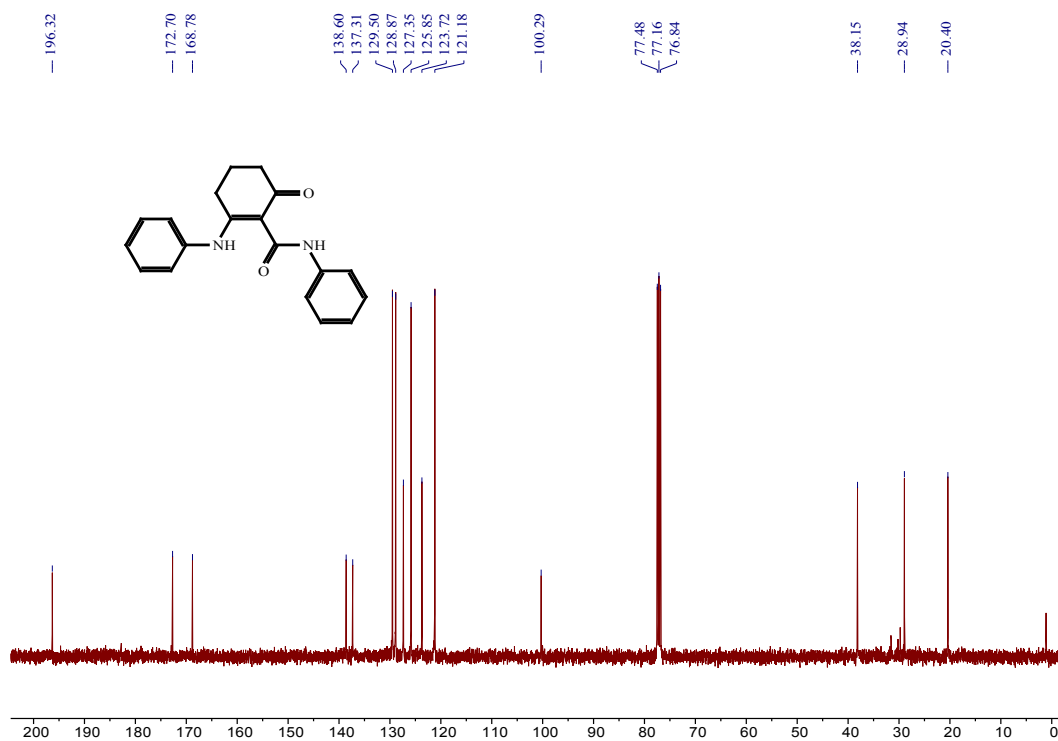


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **2e**.

6-oxo-N-phenyl-2-(phenylamino)cyclohex-1-ene-1-carboxamide (**3a**)

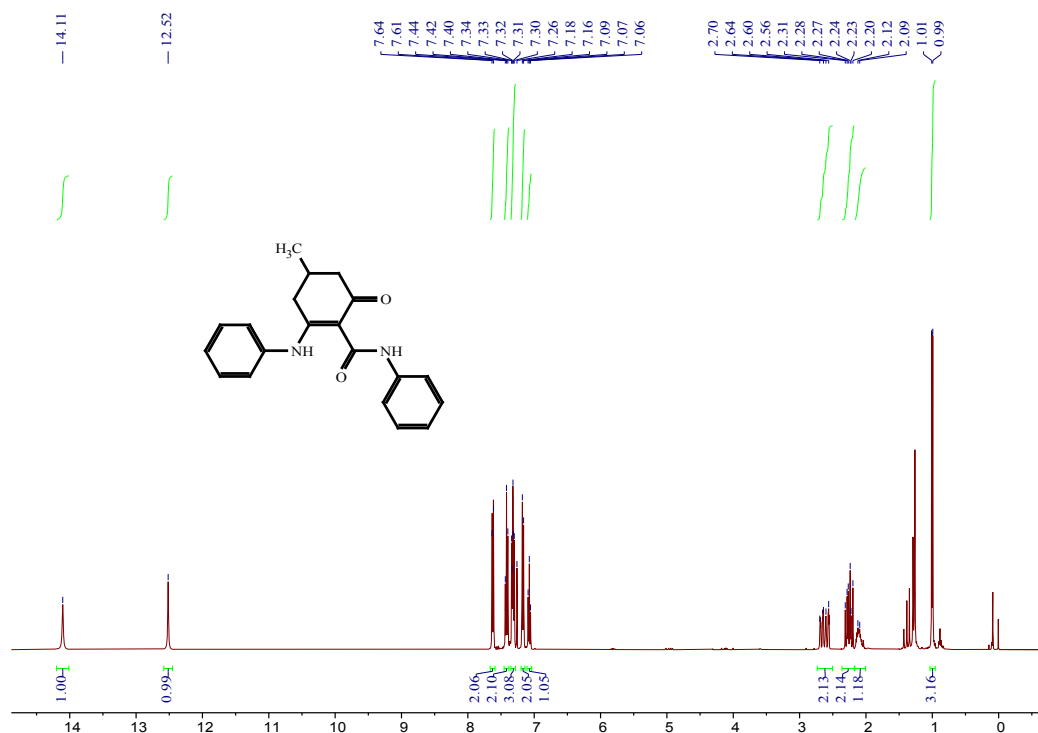


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **3a**.

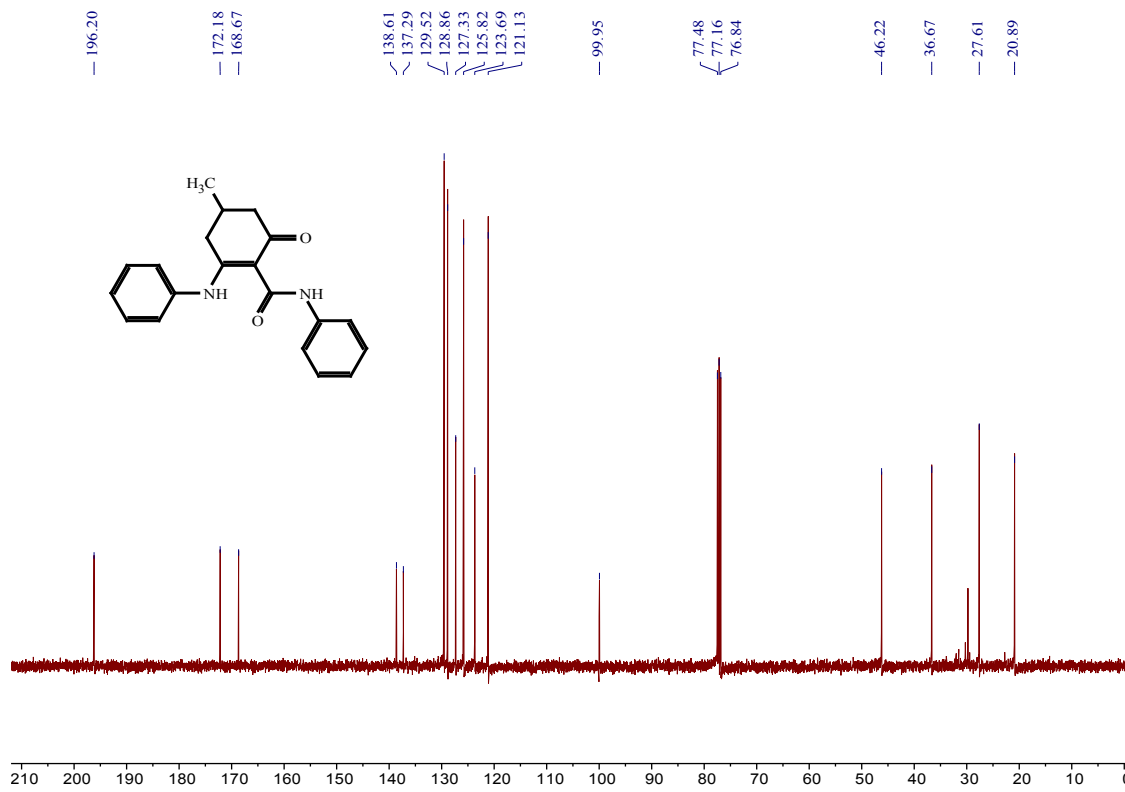


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **3a**.

4-methyl-6-oxo-N-phenyl-2-(phenylamino)cyclohex-1-ene-1-carboxamide (**3b**)

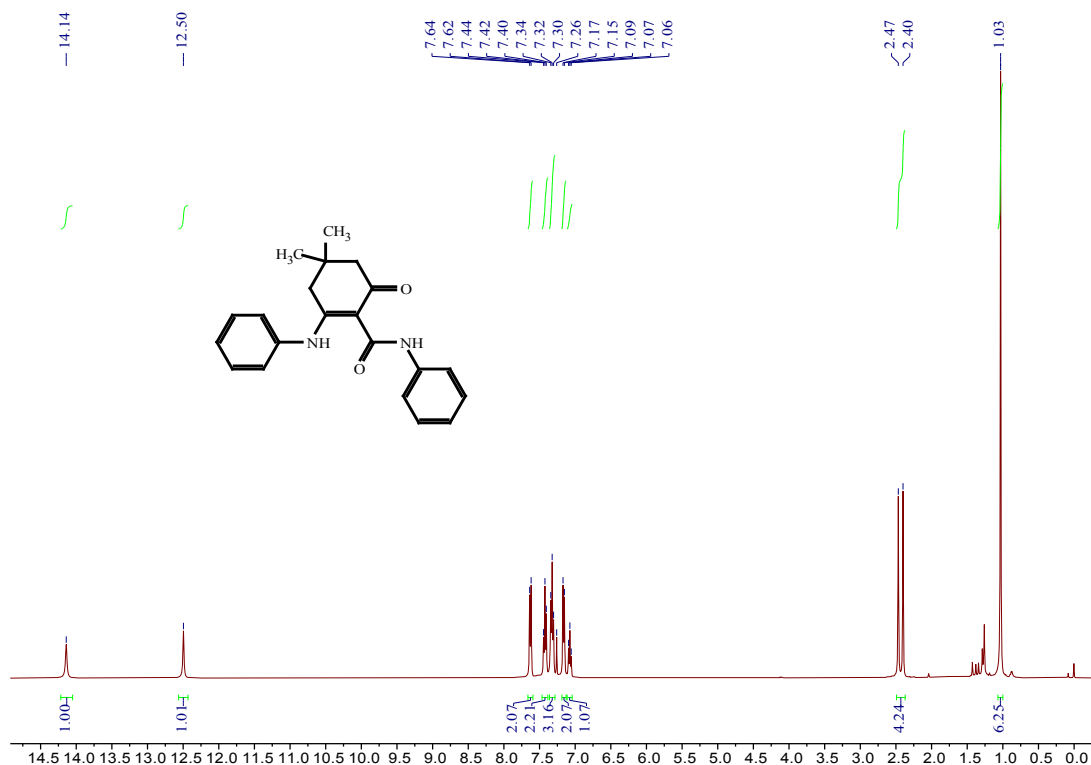


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **3b**.

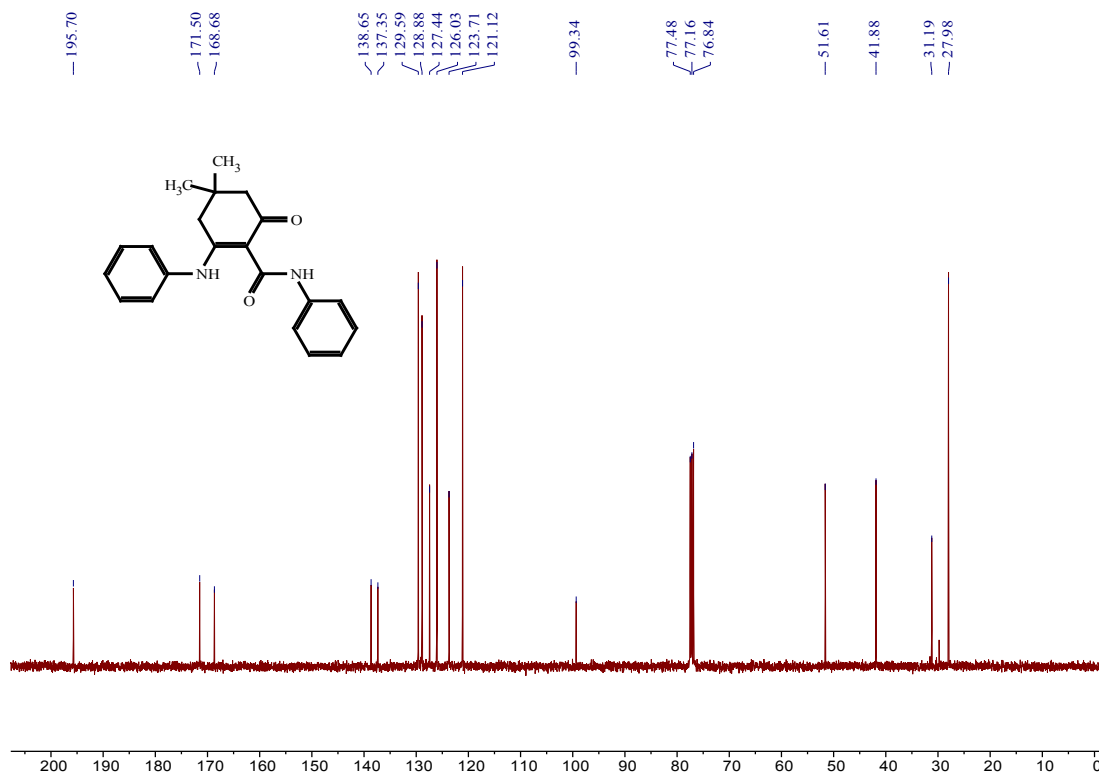


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **3b**.

4,4-dimethyl-6-oxo-N-phenyl-2-(phenylamino)cyclohex-1-ene-1-carboxamide (**3c**)

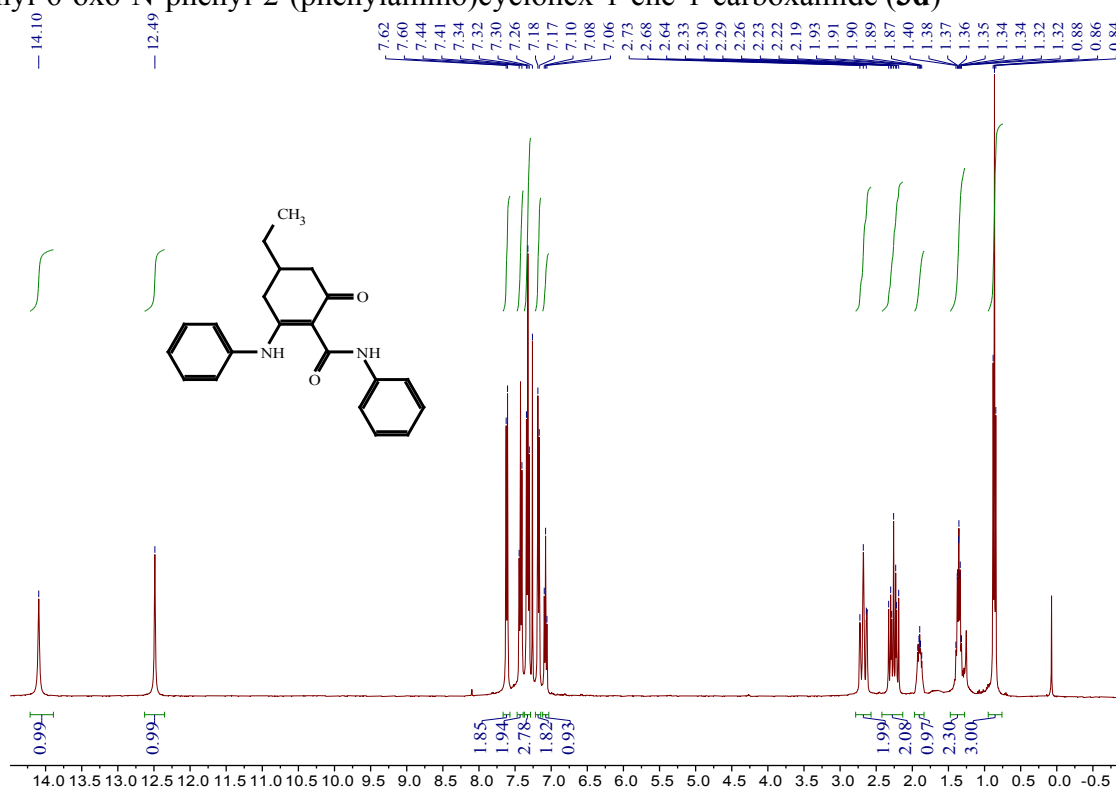


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **3c**.

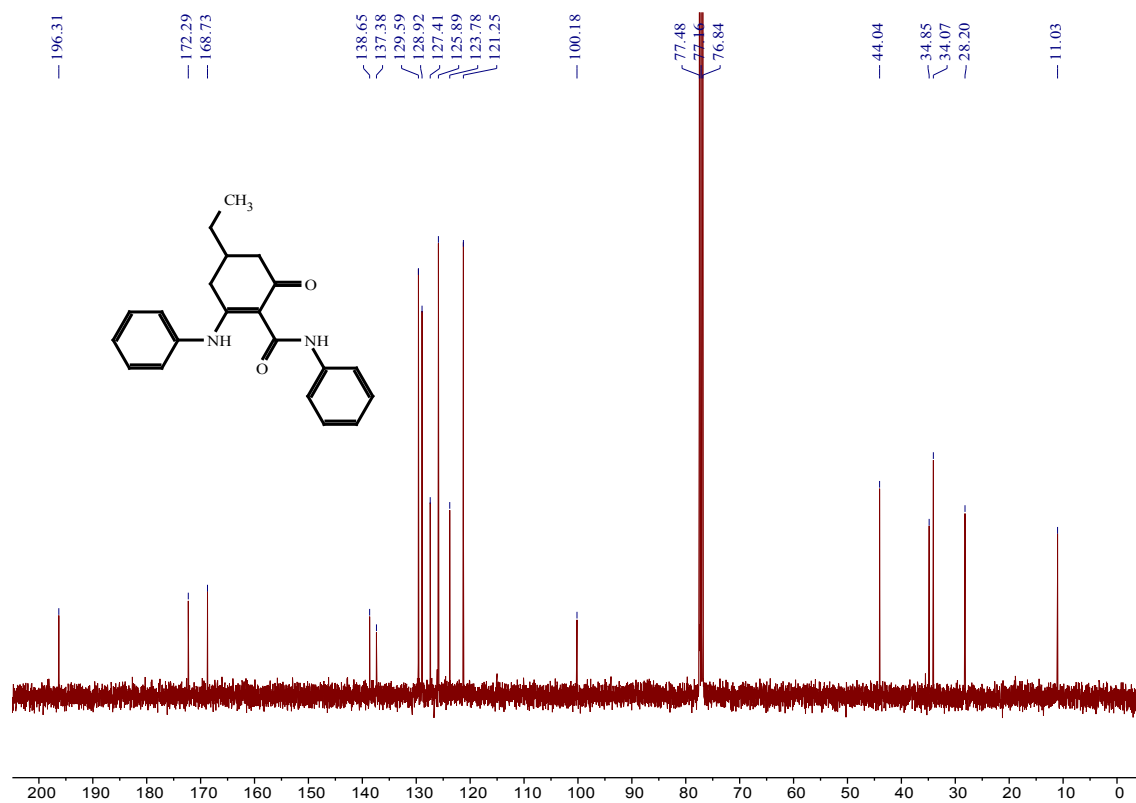


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **3c**.

4-ethyl-6-oxo-N-phenyl-2-(phenylamino)cyclohex-1-ene-1-carboxamide (**3d**)

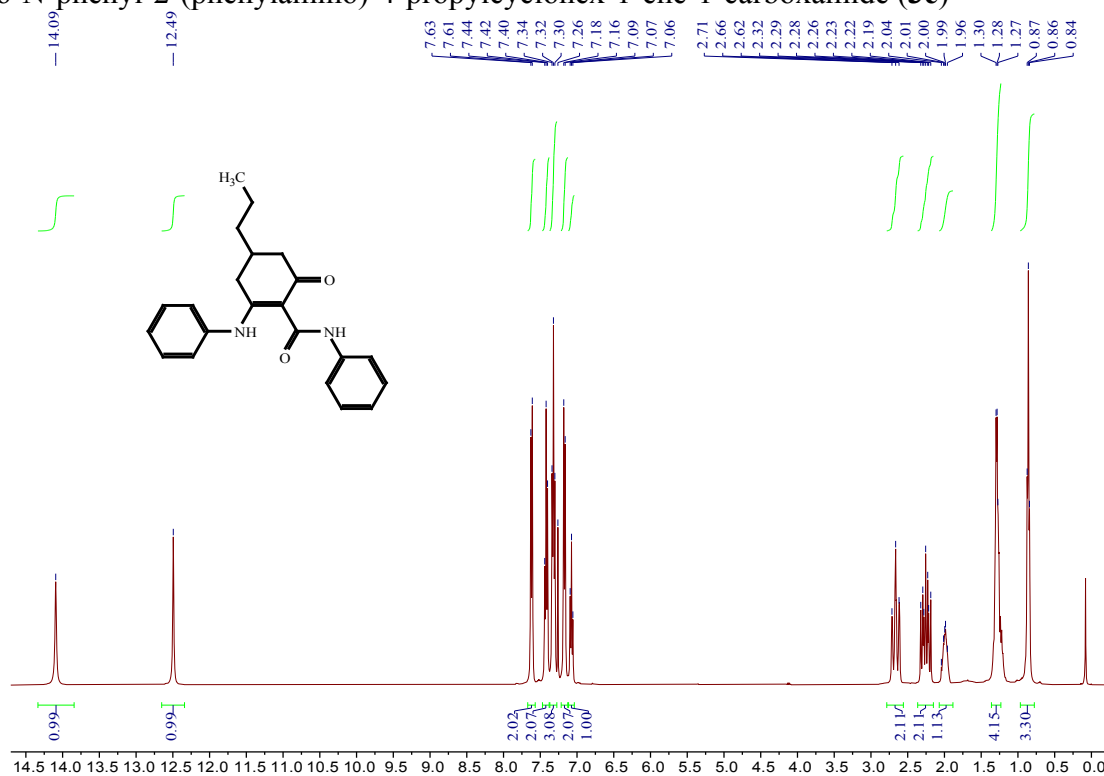


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **3d**.

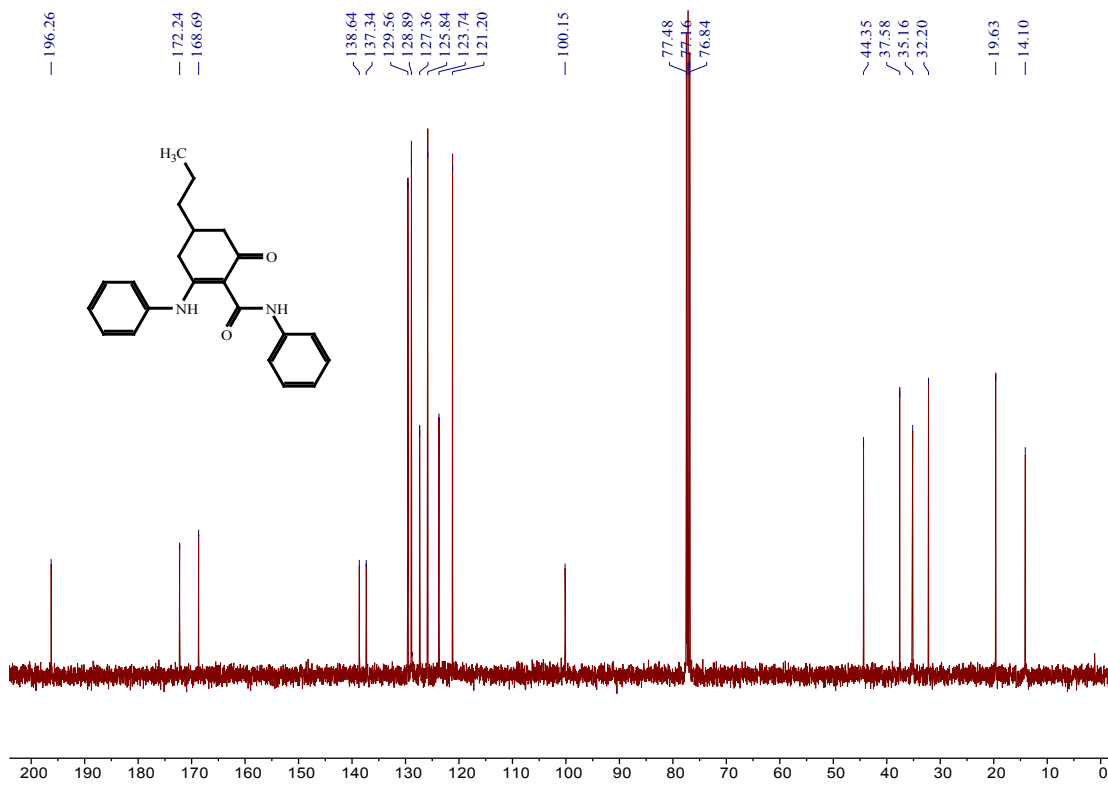


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **3d**.

6-oxo-N-phenyl-2-(phenylamino)-4-propylcyclohex-1-ene-1-carboxamide (**3e**)

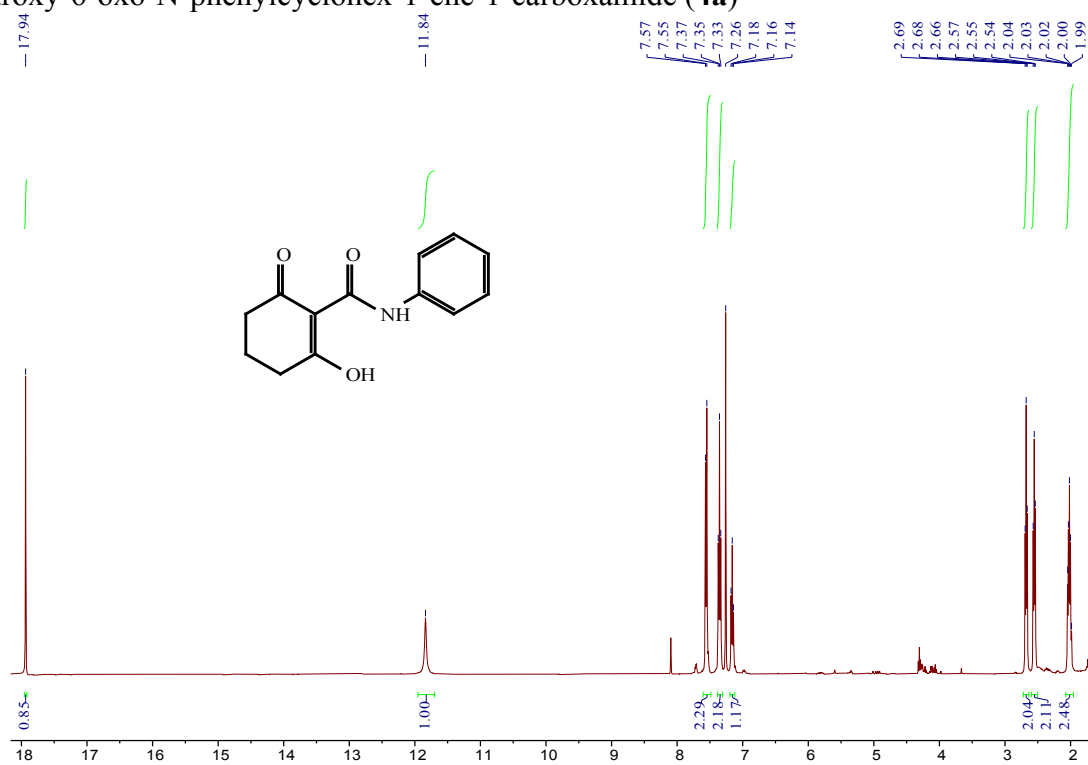


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **3e**.

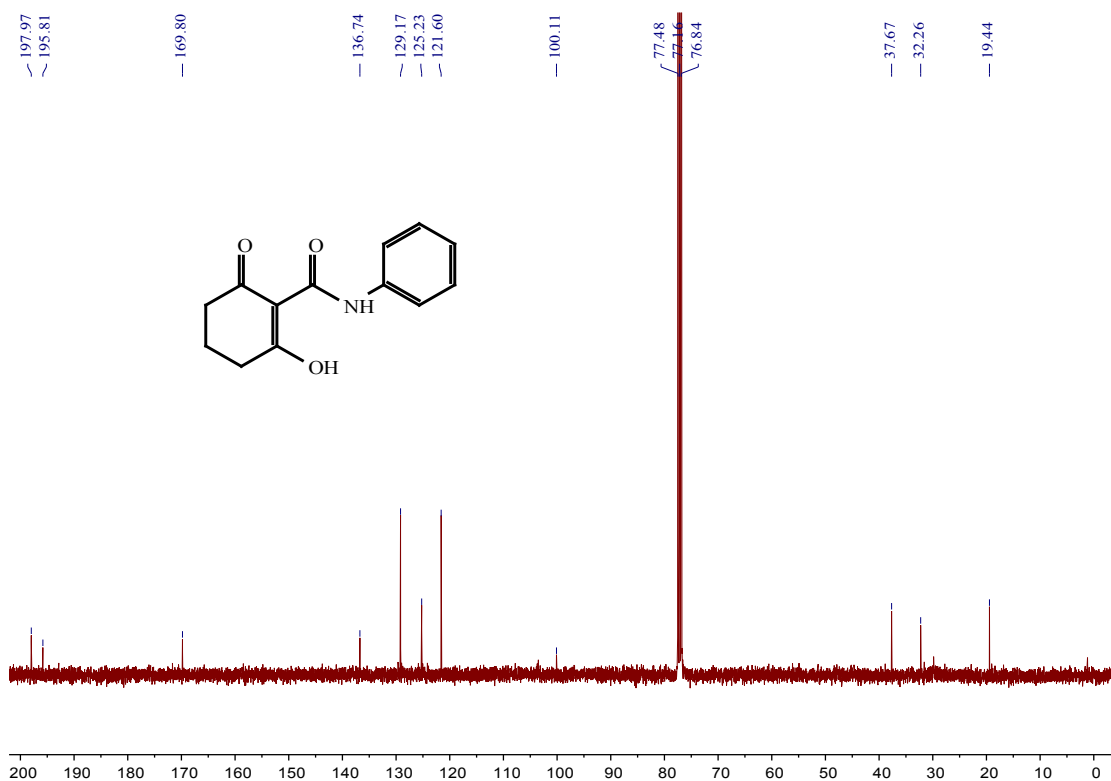


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **3e**.

2-hydroxy-6-oxo-N-phenylcyclohex-1-ene-1-carboxamide (**4a**)

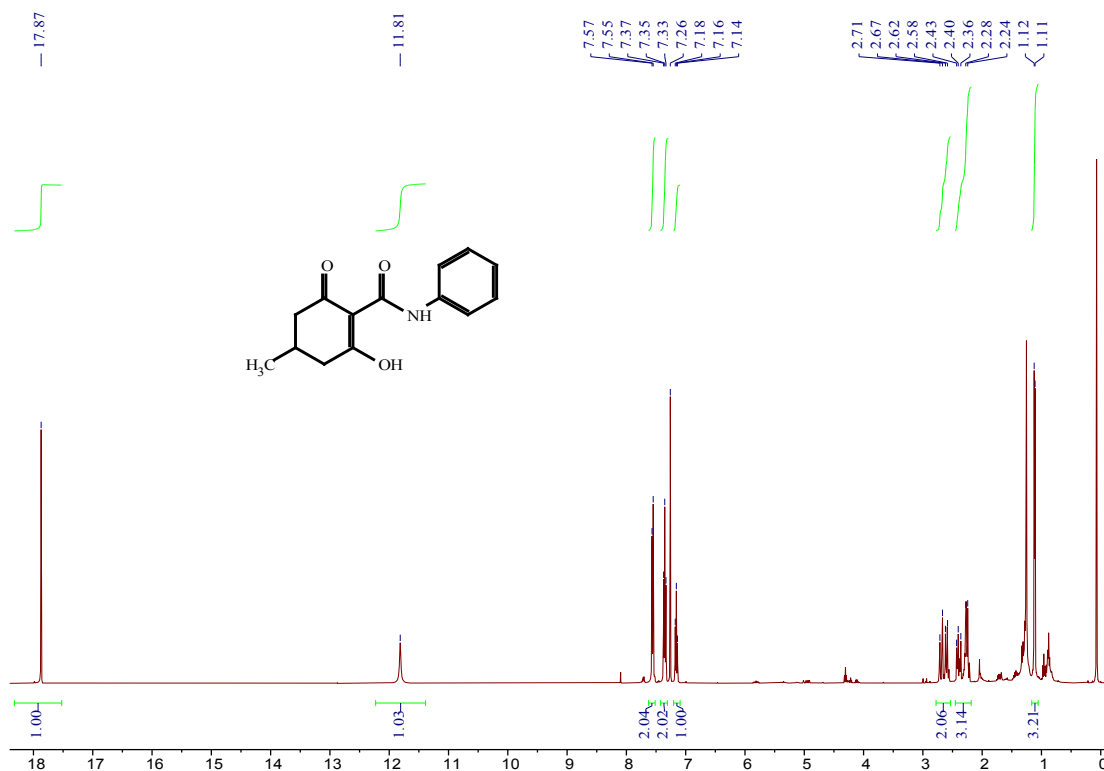


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **4a**.

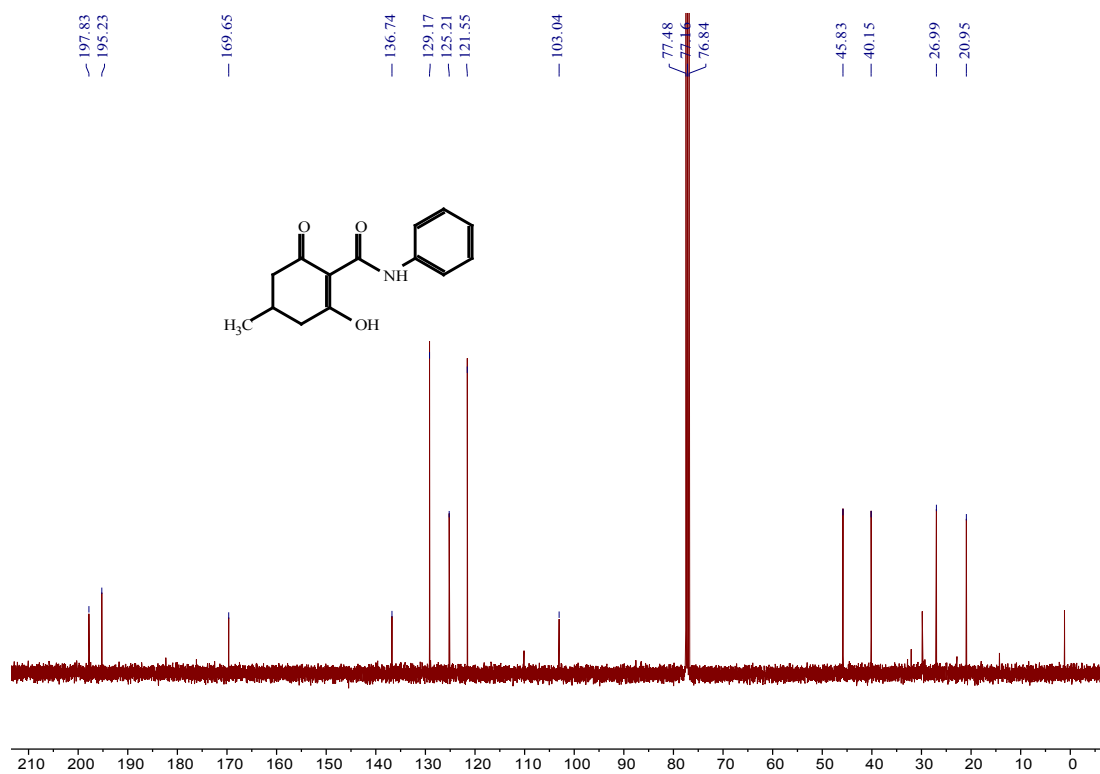


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **4a**.

2-hydroxy-4-methyl-6-oxo-N-phenylcyclohex-1-ene-1-carboxamide (**4b**)

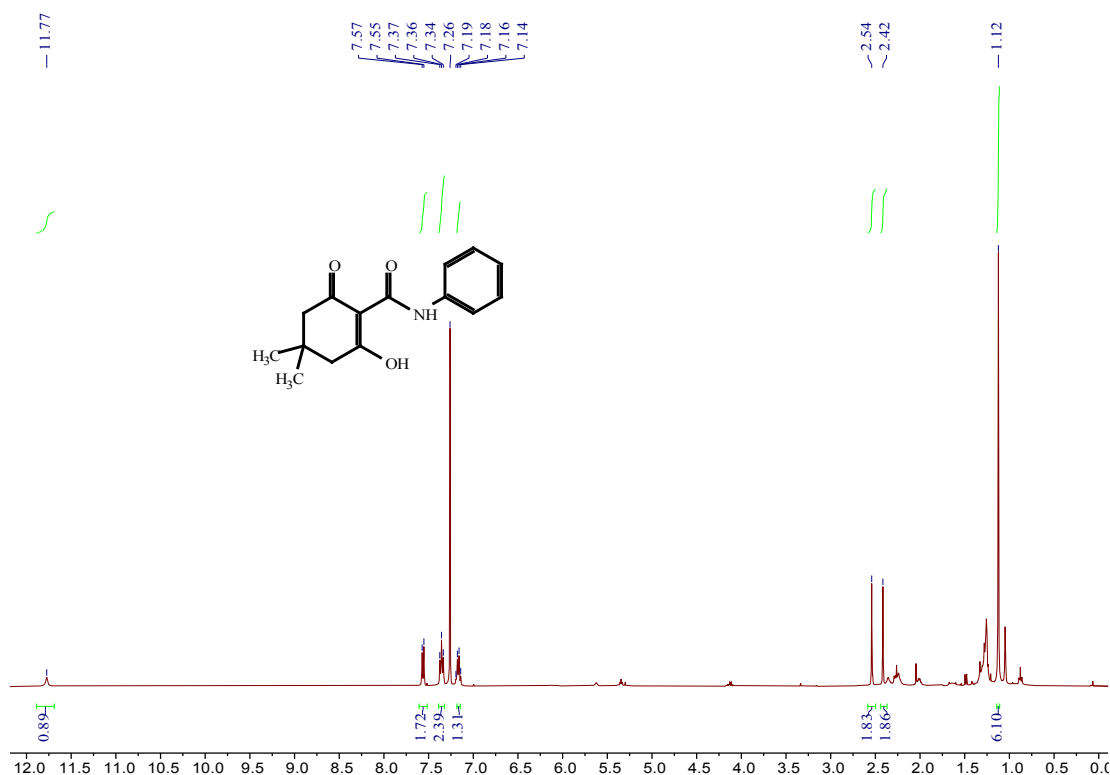


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **4b**.

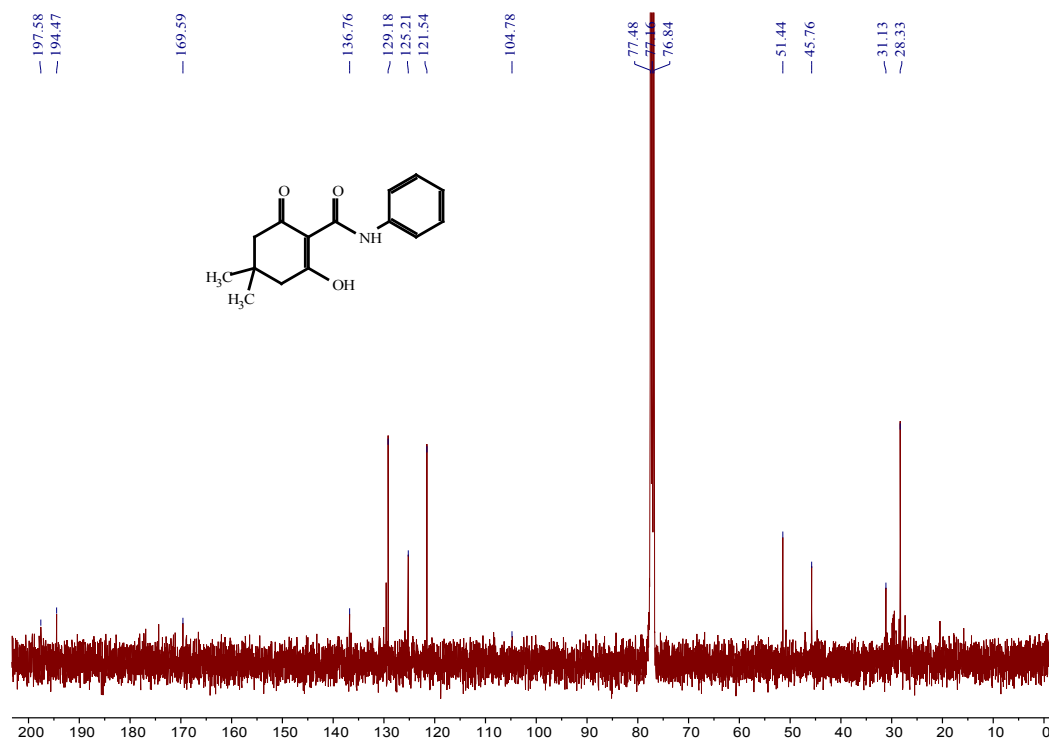


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **4b**.

2-hydroxy-4,4-dimethyl-6-oxo-N-phenylcyclohex-1-ene-1-carboxamide (**4c**)

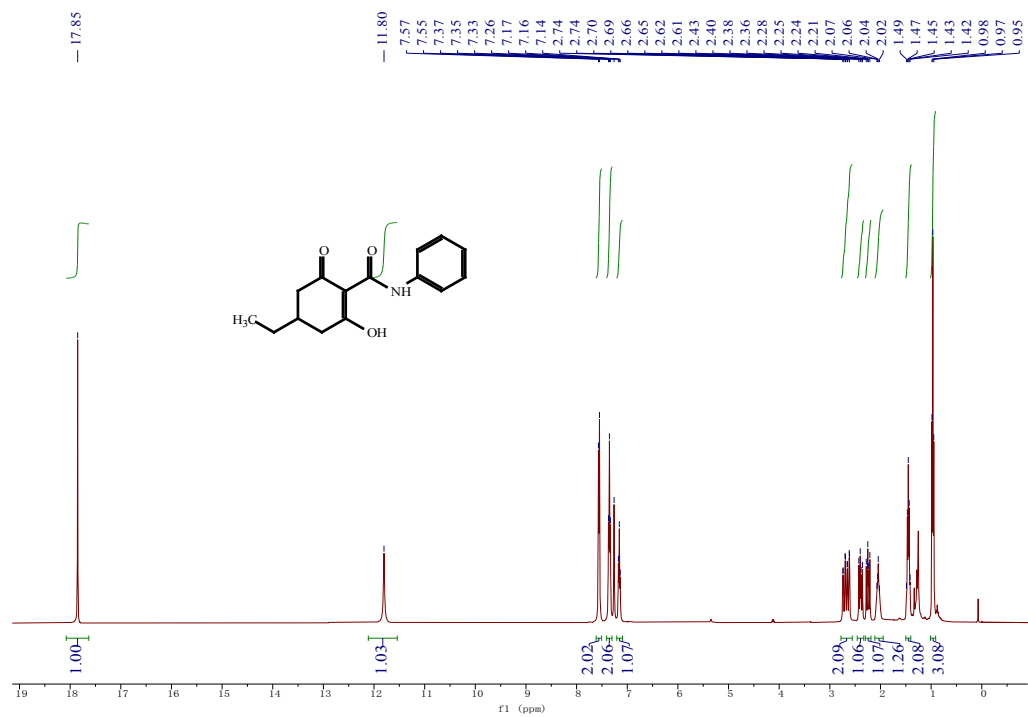


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **4c**.

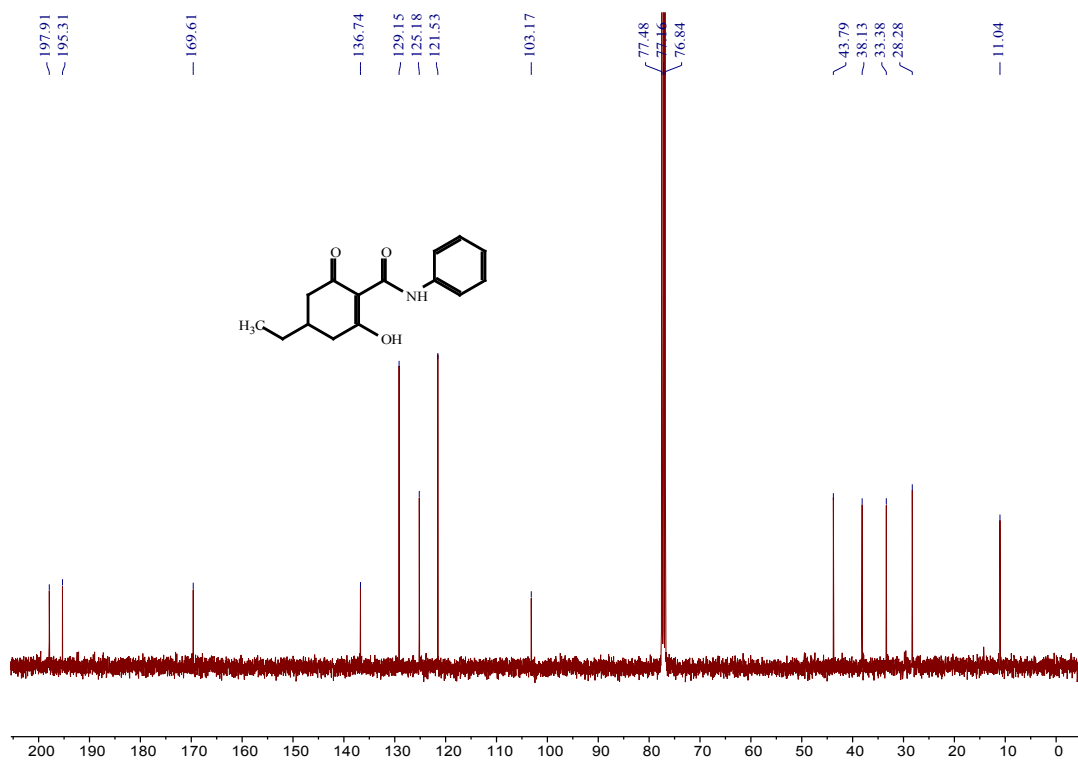


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **4c**.

4-ethyl-2-hydroxy-6-oxo-N-phenylcyclohex-1-ene-1-carboxamide (**4d**)

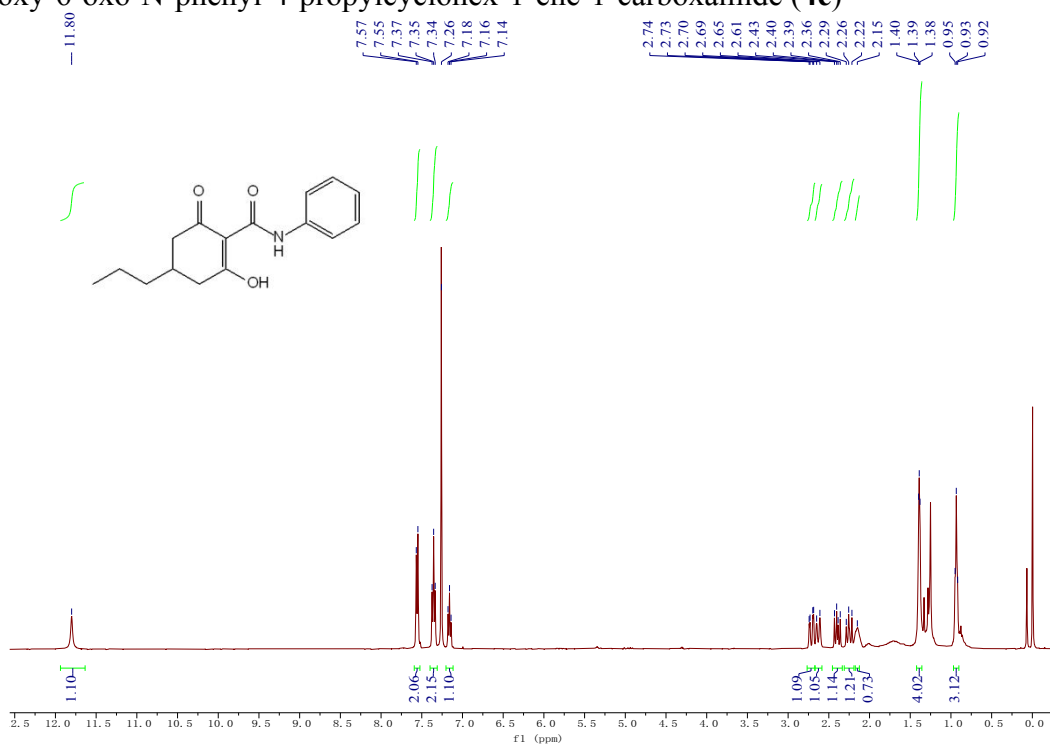


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **4d**.

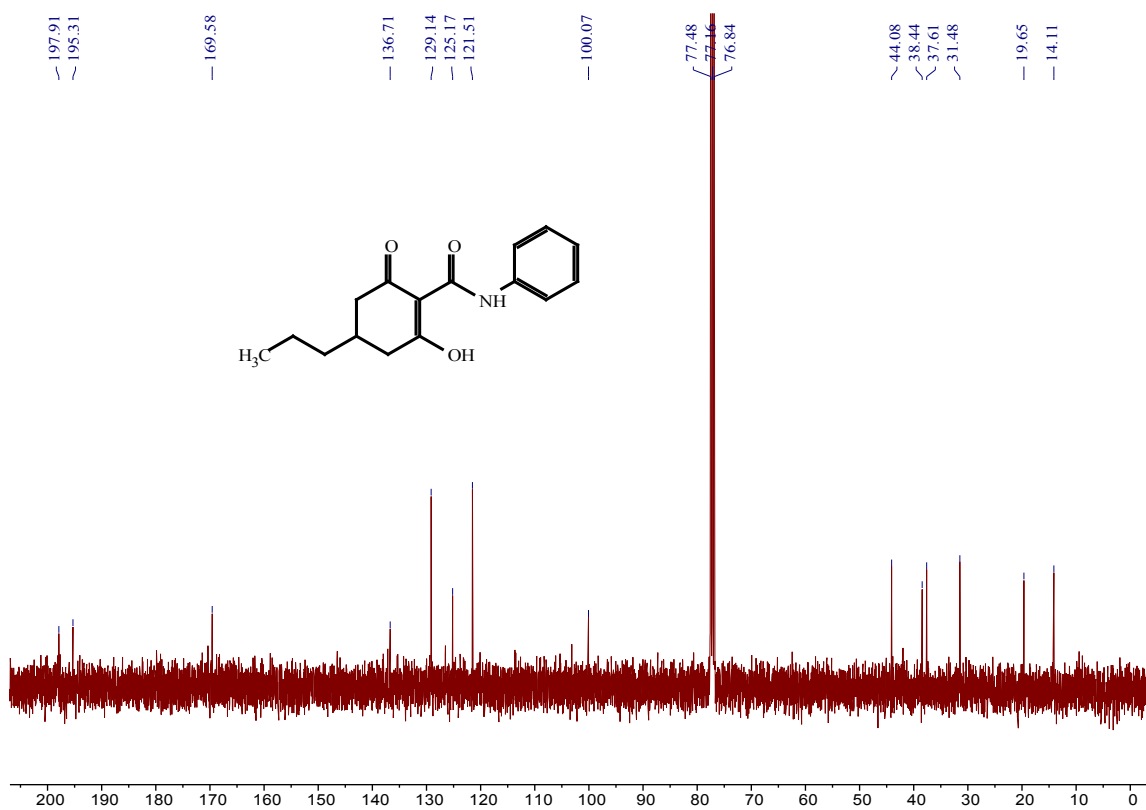


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **4d**.

2-hydroxy-6-oxo-N-phenyl-4-propylcyclohex-1-ene-1-carboxamide (**4e**)



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **4e**.**



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **4e**.**

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