

*Supporting Information*

**A Tandem Reaction Initiated by 1,4-Addition of Bis(iodozincio)methane  
for 1,3-Diketone Formation**

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## Instrumentation and Chemicals

Nuclear magnetic resonance spectra were taken on Varian UNITY INOVA 500 ( $^1\text{H}$ , 500 MHz;  $^{13}\text{C}$ , 125.7 MHz;  $^{19}\text{F}$ , 470.3 MHz) spectrometer using tetramethylsilane for  $^1\text{H}$  NMR as an internal standard ( $\delta = 0$  ppm),  $\text{CDCl}_3$  for  $^{13}\text{C}$  NMR as an internal standard ( $\delta = 77.0$  ppm) and  $\text{CFCl}_3$  for  $^{19}\text{F}$  NMR as an internal standard ( $\delta = 0$  ppm).  $^1\text{H}$  NMR spectra were also taken on Varian Mercury 300 (300 MHz) spectrometer using tetramethylsilane as an internal standard ( $\delta = 0$  ppm).  $^1\text{H}$  NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, br = broad, m = multiplet), coupling constants (Hz), and integration. High-resolution mass spectra were obtained with a JEOL JMS-700 spectrometer by electron ionization at 70 eV. Elemental analyses were carried out with a YANAKO MT2 CHN CORDER machine at Kyoto University Elemental Analysis Center. Infrared (IR) spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. Melting points were determined using a YANAKO MP-500D. TLC analyses were performed by means of Merck Kieselgel 60 F254 (0.25 mm) Plates. Visualization was accomplished with UV light (254 nm) and an aqueous vanillin solution followed by heating. Flash column chromatography was carried out using Kanto Chemical silica gel (spherical, 40–100  $\mu\text{m}$ ).

Unless otherwise noted, commercially available reagents were used without purification. Tetrahydrofuran, Dehydrated stabilizer free —Super— was purchased from Kanto Chemical Co., stored under argon, and used as it is.

## Experimental Procedures

### *General procedure for preparation of 1,3-diketone 3.*

The reaction was performed in a 20 mL round-bottomed flask filled with argon gas. Bis(iodozincio)methane (**1**, 0.6 mmol, 0.5 M in THF) was added to the solution of  $\gamma$ -acyloxy- $\alpha,\beta$ -unsaturated ketone (**2**, 0.5 mmol) in THF (2.0 mL). Then the mixture was stirred at 25 °C for 2-5 h (aryl enones: **2a-j**, **7**, **9**, **11**), and for 6-12 h (alkyl enones: **2k-n**) respectively. After an addition of saturated aqueous ammonium chloride solution, the mixture was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over sodium sulfate, and concentrated in vacuo. Purification by a flash silica gel column chromatography gave the pure corresponding 1,3-diketone **3**.

When the lactones **16** were used as substrates, the reaction mixture was stirred at 25 °C, and then at 40 °C. The reaction period were as follows: **16a** (2 h at 25 °C and 5 h at 40 °C); **16b-e** (1.5 h at 25 °C and 10 h at 40 °C). By conducted at higher temperature, the desired reaction proceeded efficiently; after treated and purified as above, the pure cyclic 1,3-diketones **17** were obtained.

### *Preparation of bis(iodozincio)methane (1).*

A mixture of pure zinc dust (25 mmol), diiodomethane (1.0 mmol), and PbCl<sub>2</sub> (0.01 mmol) in THF (2.0 mL) was sonicated for 1 h in an ultrasonic cleaner bath under Ar. When pyrometallurgy zinc dust was used instead of pure zinc, it is not necessary to add PbCl<sub>2</sub>. Both of pure zinc and pyrometallurgy zinc are commercially available. To the mixture, diiodomethane (10 mmol) in THF (20 mL) was added dropwise over 15 min at 0 °C with vigorous stirring. The mixture was stirred for 2 h at 0 °C. After the stirring was stopped, the reaction vessel was allowed to stand undisturbed for several hours. Excess zinc was separated by sedimentation. <sup>1</sup>H NMR spectra of the obtained supernatant showed a broad singlet at -1.2 ppm at 0 °C, which corresponded to the methylene proton of **1**. The supernatant was used for the further reaction as a solution of **1** in THF (0.5-0.6 M). Bis(iodozincio)methane in THF can be kept unchanged at least for a month in a sealed reaction vessel.

### *Preparation of (E)-4-oxo-4-phenylbut-2-enyl acetate (2a).*

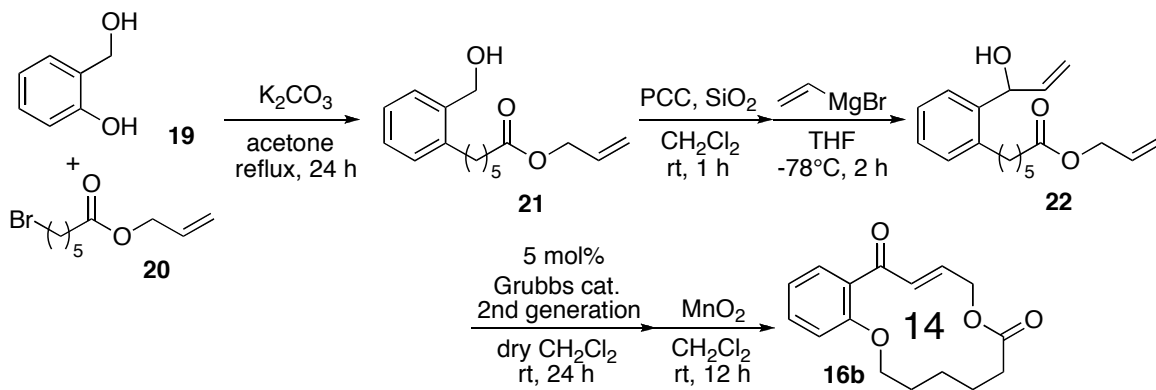
The substrate **2a** is easily obtained by an acetylation of the corresponding  $\gamma$ -hydroxy- $\alpha,\beta$ -unsaturated ketone, (*E*)-4-hydroxy-1-phenylbut-2-en-1-one, which is obtained in 4 steps from benzaldehyde in 49 % overall yield by our reported procedure.<sup>1</sup>

To a solution of (*E*)-4-hydroxy-1-phenylbut-2-en-1-one (10 mmol) in dichloromethane (10 mL), pyridine (24 mmol), acetic anhydride (12 mmol), and *N,N*-dimethyl-4-aminopyridine (0.5 mmol) were added subsequently and stirred for 12 h at 25 °C. A saturated aqueous solution of ammonium chloride was added to the reaction mixture, and then the mixture was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over sodium sulfate, and concentrated in vacuo. After a purification by a flash silica gel column chromatography (hexane/ethyl acetate = 5:1), the pure acetate **2a** was isolated in 96 % yield.

The substrates **2b-n** and **11** were also synthesized by esterifications of hydroxyenones with corresponding carboxylic anhydrides or acyl chlorides in the presence of amines. The substrates **7** and **9** were prepared by esterifications using corresponding carboxylic acids and DCC.

The precursor of the lactone **16a** was prepared by the reported procedure,<sup>2,1</sup> and its macrolactonization was performed using lipase.<sup>3</sup> The lactones **16b-e** were prepared by the following procedure.

#### *Preparation of macrolactones 16b-e.*



The substrate **16b** was obtained from commercially available 2-hydroxybenzyl alcohol (**19**) in 5 steps. Selective etherification of **19** with allyl 6-bromohexanoate (**20**) was performed by the reported procedure.<sup>4</sup> To a solution of **19** (25 mmol) in acetone (120 mL), **20** (20 mmol) and potassium carbonate (60 mmol) was added and the resulting mixture was vigorously stirred at reflux for 24 h and then cooled. After the acetone was removed under reduced pressure, the resulting residue was partitioned between ethyl acetate and 1.0 M HCl aq, and the aqueous layer was washed twice with ethyl acetate. Combined organic

layers were dried over sodium sulfate and concentrated in vacuo. After a purification by a flash silica gel column chromatography (hexane/ethyl acetate = 3:1), the corresponding pure ether **21** was obtained in 34 % yield.

**21** was oxidized by PCC with SiO<sub>2</sub> in dichloromethane at room temperature for 1 h, and the corresponding aldehyde was obtained. The aldehyde was then converted into allylic alcohol **22** by vinyl magnesium bromide in THF at -78 °C for 2 h. A purification by a flash silica gel column chromatography (hexane/ethyl acetate = 10:1) gave pure **22** in 44 % yield in 2 steps.

After a solution of **22** in dry dichloromethane (0.01 M) was bubbled with argon gas for 20 minutes, 5 mol% of Grubbs catalyst 2nd generation was added and stirred at room temperature for 24 h.<sup>5</sup> The catalyst was removed by a filtration and 14-membered lactone was obtained. Oxidation using MnO<sub>2</sub> in dichloromethane at room temperature for 12 h and purification by a flash silica gel column chromatography (hexane/ethyl acetate = 3:1) gave the substrate **16b** in 67 % yield in 2 steps.

The substrates **16c-e** were also obtained in the same way using the corresponding allyl esters instead of **20**.

### References

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3. Makita, A.; Nihira, T.; Yamada, Y. *Tetrahedron Lett.* **1987**, *28*, 805-808.
4. Shotwell, J. B.; Krygowski, E. S.; Hines, J.; Koh, B.; Huntsman, E. W. D.; Choi, H. W.; Schneekloth, Jr., J. S.; Wood, J. L.; Crews, C. M. *Org. Lett.* **2002**, *4*, 3087-3089.
5. Brenneman, J. B.; Machauer, R.; Martin, S. F. *Tetrahedron*, **2004**, *60*, 7301-7314.

### **<sup>1</sup>H NMR Analyses of Reactions using Dideuteriobis(iodozincio)methane (1-D)**

To investigate the pathway of our tandem reaction, two experiments were conducted as follows: one was a treatment of (*E*)-4-oxo-4-phenylbut-2-enyl acetate (**2a**) with bis(iodozincio)methane (**1**) using THF-*d*<sub>8</sub> as a solvent, and the other was that of **2a** with dideuteriobis(iodozincio)methane (**1-D**) using THF-*d*<sub>8</sub> as a solvent. By comparing <sup>1</sup>H NMR spectra of these reaction mixtures, the formation of 2-propen-1-ol (**4**) and 3,3-dideuterio-2-propen-1-ol (**4-D**) was confirmed respectively.

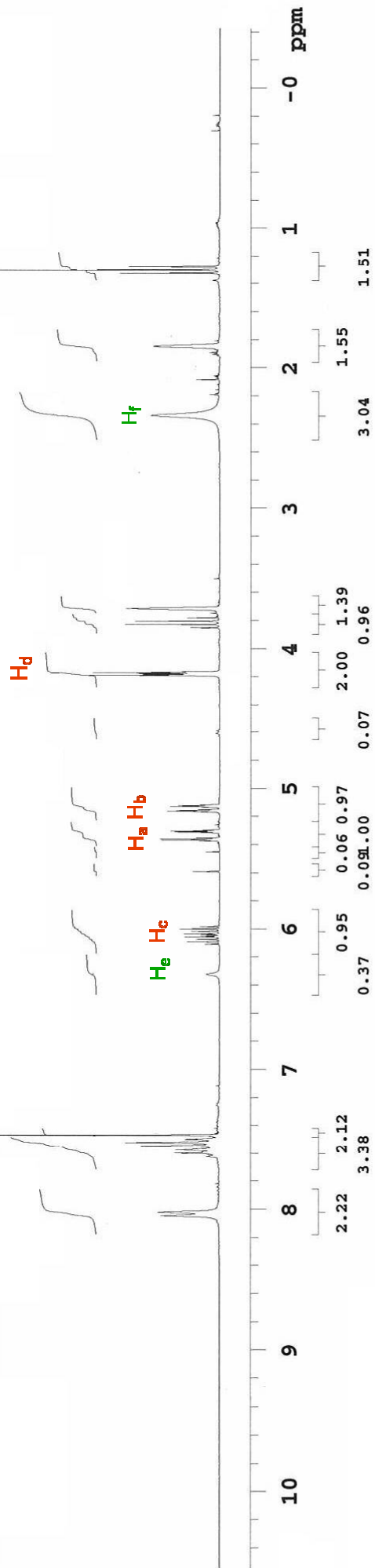
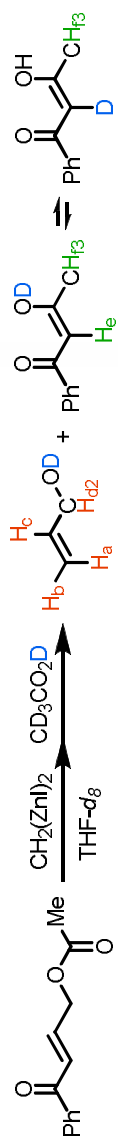
The reaction was performed in a 20 mL round-bottomed flask filled with argon gas. Bis(iodozincio)methane (**1**, 0.6 mmol, 0.5 M in THF-*d*<sub>8</sub>) or dideuteriobis(iodozincio)methane (**1-D**, 0.6 mmol, 0.5 M in THF-*d*<sub>8</sub>) was added to the solution of (*E*)-4-oxo-4-phenylbut-2-enyl acetate (**2a**, 0.5 mmol) in THF-*d*<sub>8</sub> (2.0 mL). Then the mixture was stirred for 2 h at 25 °C. After being quenched with acetic acid-*d*<sub>4</sub>, the resulting mixture gave the following <sup>1</sup>H NMR spectra.

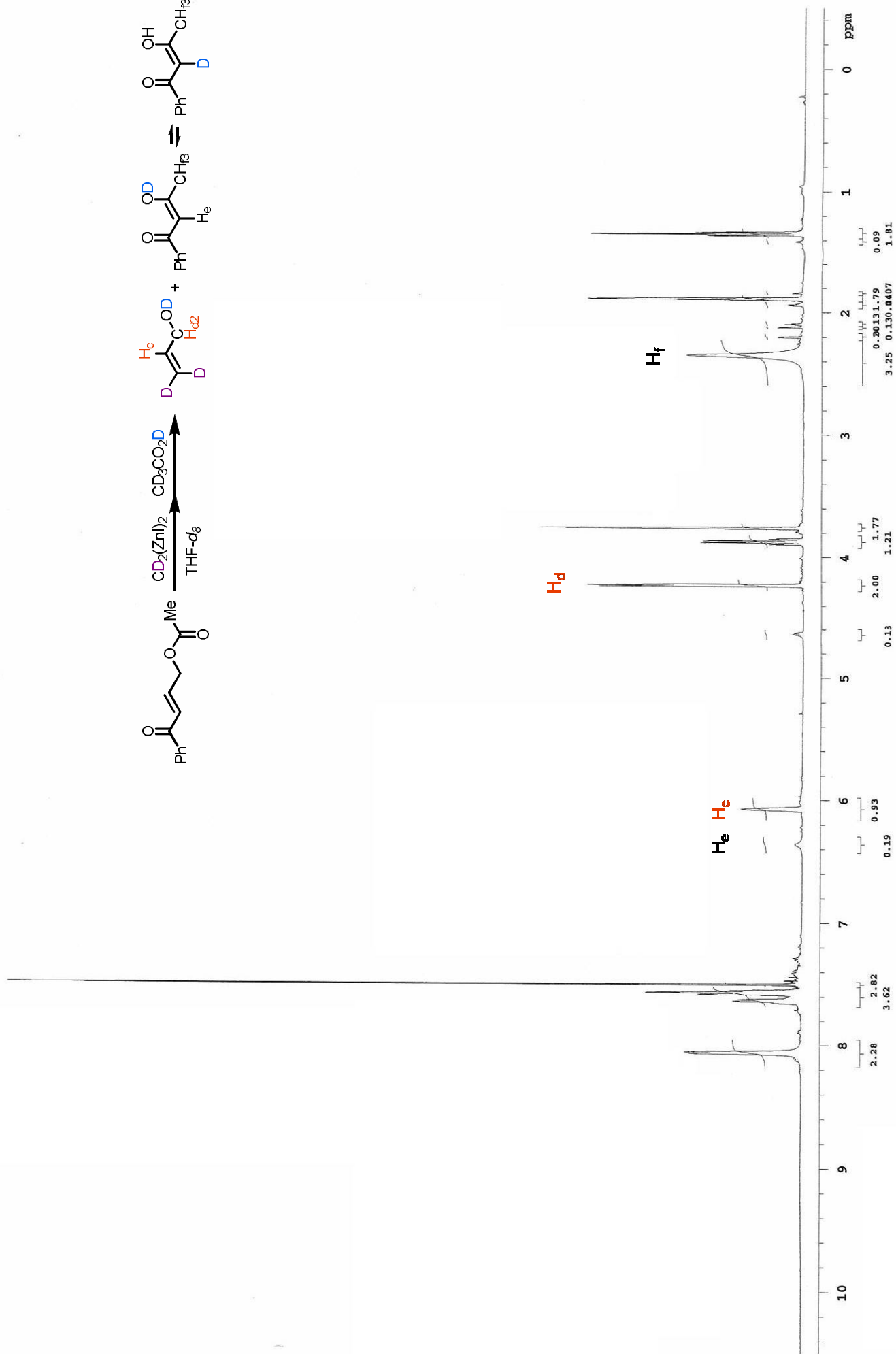
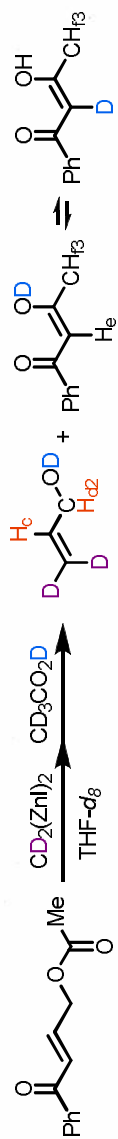
From these spectra, the formation of 2-propen-1-ol (**4**) and 3,3-dideuterio-2-propen-1-ol (**4-D**) were identified. From these observations, the released allyl alcohol (**4**) contained the methylene group from the dizinc reagent **1**.

The formation of the desired product, 1-phenylbutane-1,3-dione (**3a**) was also detected from these spectra. Some of the hydrogen atoms at 2-position were exchanged with the acidic deuterium atoms of acetic acid-*d*<sub>4</sub> via a keto-enol equilibrium as shown in the scheme on the spectra.

<sup>1</sup>H NMR spectrum (300 MHz) of the reaction mixture of **2a** and **1** in THF-*d*<sub>8</sub> (S-7).

<sup>1</sup>H NMR spectrum (500 MHz) of the reaction mixture of **2a** and **1-D** in THF-*d*<sub>8</sub> (S-8).





## Characterization Data of the Substrates and the Products

The products are in keto-enol equilibrium, so characterization data of only major form of each product are shown. Major form of each product is written in the parentheses.

### (*E*)-4-Oxo-4-phenylbut-2-enyl acetate (2a): CAS RN [127391-77-9]

Yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.96 – 7.93 (m, 2H), 7.58 (tt, *J* = 7.5, 2.0 Hz, 1H), 7.51 – 7.47 (m, 2H), 7.09 (dt, *J* = 15.5, 1.5 Hz, 1H), 7.01 (dt, *J* = 15.5, 4.5 Hz, 1H), 4.85 (dd, *J* = 4.5, 1.5 Hz, 2H), 2.16 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 190.0, 170.4, 141.1, 137.4, 133.1, 128.65, 128.61, 126.0, 63.2, 20.8.

### 1-Phenylbutane-1,3-dione (3a): CAS RN [93-91-4]

Yield: 91 %, white solid. (enol form) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.90 – 7.87 (m, 2H), 7.52 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.47 – 7.43 (m, 2H), 6.18 (s, 1H), 2.21 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 193.8, 183.3, 134.9, 132.3, 128.6, 127.0, 96.7, 25.9.

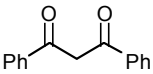
### 4-Methyl-1-phenylpentane-1,3-dione (3b): CAS RN [13988-65-3]

Yield: 91 %, colorless oil. (enol form) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.91 – 7.88 (m, 2H), 7.52 (tt, *J* = 6.5, 1.5 Hz, 1H; CH), 7.48 – 7.43 (m, 2H), 6.19 (s, 1H), 2.62 (sept, *J* = 7.0 Hz, 1H), 1.23 (d, *J* = 7.0 Hz, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 201.2, 183.8, 135.2, 132.2, 128.6, 126.9, 94.2, 37.5, 19.4.

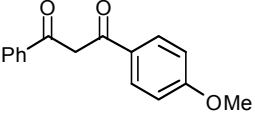
### 4,4-Dimethyl-1-phenylpentane-1,3-dione (3c): CAS RN [13988-67-5]

Yield: 81 %, colorless oil. (enol form) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.91 – 7.87 (m, 2H), 7.52 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.47 – 7.44 (m, 2H), 6.31 (s, 1H), 1.26 (s, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 202.9, 184.6, 135.5, 132.1, 128.6, 127.0, 92.1, 39.9, 27.4.

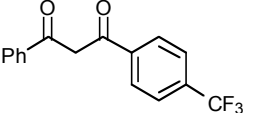
**1,3-diphenylpropane-1,3-dione (3d):** CAS RN [120-46-7]

 Yield: 97 %, white solid. (enol form)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 – 7.98 (m, 4H), 7.56 (tt,  $J = 7.5, 1.5$  Hz, 2H), 7.52 – 7.48 (m, 4H), 6.87 (s, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  185.8, 135.6, 132.4, 128.7, 127.2, 93.2.

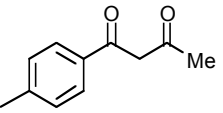
**1-*p*-Methoxyphenyl-3-phenylpropane-1,3-dione (3e):** CAS RN [6327-79-3]

 Yield: >99 %, white solid. (enol form)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 – 7.96 (m, 4H), 7.54 (tt,  $J = 7.5, 1.5$  Hz, 1H), 7.51 – 7.46 (m, 2H), 7.00 – 6.97 (m, 2H), 6.80 (s, 1H), 3.89 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  186.2, 184.0, 163.2, 135.5, 132.2, 129.3, 128.6, 128.2, 127.0, 114.0, 92.4, 55.5.

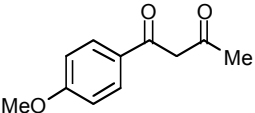
**1-*p*-Trifluoromethylphenyl-3-phenylpropane-1,3-dione (3f):** CAS RN [129700-38-5]

 Yield: 95 %, white solid. (enol form)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.10 – 8.08 (m, 2H), 8.02 – 7.95 (m, 2H), 7.78 – 7.74 (m, 2H), 7.59 (tt,  $J = 7.5, 1.5$  Hz, 1H), 7.54 – 7.50 (m, 2H), 6.88 (s, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  187.0, 183.4, 138.7, 135.3, 133.7 (q,  $J = 32$  Hz), 132.9, 128.8, 127.4, 127.3, 125.7 (q,  $J = 3.9$  Hz), 123.7 (q,  $J = 271$  Hz), 93.7.  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ )  $\delta$  –63.4.

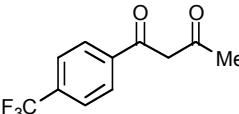
**1-*p*-Tolylbutane-1,3-dione (3g):** CAS RN [4023-79-4]

 Yield: 92 %, pale yellow oil. (enol form)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78 (dt,  $J = 8.5, 2.0$  Hz, 2H), 7.25 (d,  $J = 8.5$  Hz, 2H), 6.15 (s, 1H), 2.40 (s, 3H), 2.18 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  193.0, 183.7, 143.0, 132.1, 129.3, 127.0, 96.3, 25.6, 21.6.

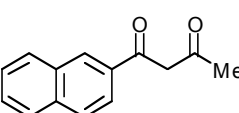
**1-*p*-Methoxyphenylbutane-1,3-dione (3h):** CAS RN [4023-80-7]

 Yield: 84 %, white solid. (enol form)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 (ddd,  $J = 9.5, 2.5, 2.5$  Hz, 2H), 6.94 (ddd,  $J = 9.5, 2.5, 2.5$  Hz, 2H), 6.12 (s, 1H), 3.87 (s, 3H), 2.17 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  191.6, 184.1, 163.1, 131.1, 129.1, 113.9, 95.8, 55.4, 25.3.

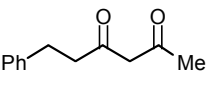
**1-*p*-Trifluoromethylphenylbutane-1,3-dione (3i):** CAS RN [258346-69-9]

 Yield: 91 %, white solid. (enol form)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (d,  $J = 8.0$  Hz, 2H), 7.70 (d,  $J = 8.0$  Hz, 2H), 6.20 (s, 1H), 2.24 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  195.1, 180.9, 138.1, 133.6 (q,  $J = 32$  Hz), 127.3, 125.6 (q,  $J = 3.6$  Hz), 123.7 (q,  $J = 271$  Hz), 97.4, 26.2.  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -63.4.

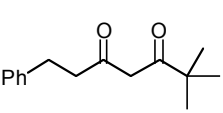
**1-(Naphthalen-2-yl)butane-1,3-dione (3j):** CAS RN [13298-50-5]

 Yield: 91 %, pale yellow solid. (enol form)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.44 (s, 1H), 7.95 – 7.85 (m, 4H), 7.59 – 7.52 (m, 2H), 6.32 (s, 1H), 2.24 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  193.8, 183.1, 135.2, 132.7, 132.0, 129.2, 128.3, 128.1, 128.0, 127.7, 126.7, 123.0, 97.0, 25.9.

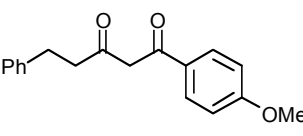
**6-Phenylhexane-2,4-dione (3k):** CAS RN [52393-50-7]

 Yield: 55 %, colorless oil. (enol form)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 – 7.27 (m, 2H), 7.23 – 7.17 (m, 3H), 5.48 (s, 1H), 2.94 (t,  $J = 8.0$  Hz, 2H), 2.60 (t,  $J = 8.0$  Hz, 2H), 2.04 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  193.2, 191.0, 140.7, 128.5, 128.3, 126.2, 100.0, 40.0, 31.5, 24.8.

**2,2-Dimethyl-7-phenylheptane-3,5-dione (3l):**

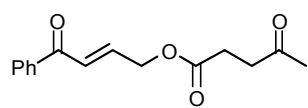
 Yield: 61 %, white solid. (enol form) TLC:  $R_f$  0.82 (hexane/ethyl acetate = 3:1). Mp. 105 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 – 7.26 (m, 2H), 7.22 – 7.17 (m, 3H), 5.54 (s, 1H), 2.95 (t,  $J = 8.0$  Hz, 2H), 2.63 (t,  $J = 8.0$  Hz, 2H), 1.14 (s, 9H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  200.1, 194.4, 140.8, 128.5, 128.3, 126.2, 95.4, 40.5, 39.0, 31.7, 27.2. IR (KBr): 3545, 2960, 2924, 2850, 1730, 1719, 1602, 1458, 1263, 1098, 799, 741, 700  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{15}\text{H}_{20}\text{O}_2$ : C, 77.55; H, 8.68. Found: C, 77.28; H, 8.75.

**1-*p*-Methoxyphenyl-5-phenylpentane-1,3-dione (3m):**

 Yield: 69 %, white solid. (enol form) TLC:  $R_f$  0.60 (hexane/ethyl acetate = 3:1). Mp. 64 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 – 7.82 (m, 2H), 7.32 – 7.28 (m, 2H), 7.24 – 7.21

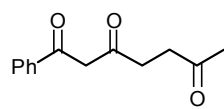
(m, 3H), 6.96 – 6.92 (m, 2H), 6.08 (s, 1H), 3.87 (s, 3H), 3.01 (t,  $J = 8.0$  Hz, 2H), 2.72 (t,  $J = 8.0$  Hz, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  193.6, 184.0, 163.1, 140.8, 131.1, 129.1, 128.5, 128.3, 126.2, 113.9, 95.4, 55.4, 40.5, 31.8. IR (KBr): 4060, 3026, 2930, 1603, 1560, 1499, 1451, 1260, 1182, 1032, 789, 700  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{18}\text{H}_{18}\text{O}_3$ : C, 76.57; H, 6.43. Found: C, 76.56; H, 6.64.

**(E)-4-Oxo-4-phenylbut-2-enyl 4-oxopentanoate (7):**



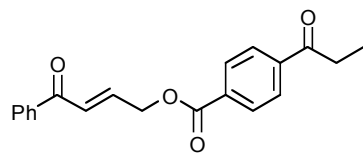
Pale orange solid. TLC:  $R_f$  0.16 (hexane/ethyl acetate = 3:1). Mp. 68 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 – 7.97 (m, 2H), 7.58 (tt,  $J = 7.5, 1.5$  Hz, 1H), 7.51 – 7.47 (m, 2H), 7.13 (dt,  $J = 15.5, 2.0$  Hz, 1H), 7.01 (dt,  $J = 15.5, 4.5$  Hz, 1H), 4.87 (dd,  $J = 4.5, 2.0$  Hz, 2H), 2.82 (t,  $J = 6.5$  Hz, 2H), 2.69 (t,  $J = 6.5$  Hz, 2H), 2.22 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  206.4, 189.9, 172.2, 140.9, 137.4, 133.1, 128.7, 128.6, 125.8, 63.3, 37.9, 29.8, 27.8. IR (KBr): 2359, 2342, 1738, 1715, 1670, 1630, 1304, 1155, 758, 692  $\text{cm}^{-1}$ . HRMS Calcd for  $\text{C}_{15}\text{H}_{16}\text{O}_4$ :  $M^+$ , 260.1049. Found:  $m/z$  260.1047.

**1-Phenylheptane-1,3,6-trione (8):** CAS RN [100330-42-5]

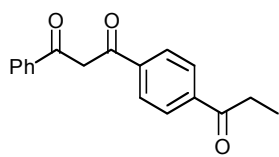


Yield: 74 %, pale yellow oil. (enol form)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 – 7.86 (m, 2H), 7.53 – 7.43 (m, 3H), 6.20 (s, 1H), 2.84 (t,  $J = 6.5$  Hz, 2H), 2.77 (t,  $J = 6.5$  Hz, 2H), 2.22 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  206.9, 197.8, 180.0, 134.2, 132.2, 128.6, 126.8, 96.4, 37.9, 33.5, 29.9.

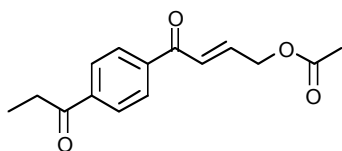
**(E)-4-Oxo-4-phenylbut-2-enyl 4-propionylbenzoate (9):**



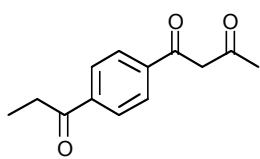
White solid. TLC:  $R_f$  0.33 (hexane/ethyl acetate = 3:1). Mp. 112 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.19 (ddd,  $J = 8.5, 2.0, 1.5$  Hz, 2H), 8.05 (ddd,  $J = 8.5, 2.0, 1.5$  Hz, 2H), 7.96 – 7.93 (m, 2H), 7.34 (tt,  $J = 7.5, 1.5$  Hz, 1H), 7.52 – 7.47 (m, 2H), 7.18 (dt,  $J = 15.5, 1.5$  Hz, 1H), 7.12 (dt,  $J = 15.5, 4.5$  Hz, 1H), 5.46 (dd,  $J = 4.5, 1.5$  Hz, 2H), 3.05 (q,  $J = 7.0$  Hz, 2H), 1.25 (t,  $J = 7.0$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  200.2, 189.9, 165.1, 140.7, 140.5, 137.3, 133.2, 133.1, 130.0, 128.7, 128.6, 128.0, 126.4, 64.0, 32.2, 8.0. IR (KBr): 1713, 1684, 1620, 1285, 1219, 1128, 762, 691  $\text{cm}^{-1}$ . HRMS Calcd for  $\text{C}_{20}\text{H}_{18}\text{O}_4$ :  $M^+$ , 322.1205. Found:  $m/z$  322.1201.

**1-Phenyl-3-(4-propionylphenyl)propane-1,3-dione (10):**

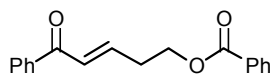
Yield: 97 %, pale yellow solid. (enol form) TLC:  $R_f$  0.55 (hexane/ethyl acetate = 3:1). Mp. 153 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 (s, 4H), 8.02 – 8.00 (m, 2H), 7.62 – 7.57 (m, 1H), 7.54 – 7.49 (m, 2H), 6.90 (s, 1H), 3.06 (q,  $J$  = 7.0 Hz, 2H), 1.26 (t,  $J$  = 7.0 Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  200.1, 187.1, 183.3, 139.5, 139.0, 135.4, 132.8, 128.7, 128.2, 127.29, 127.25, 93.8, 32.1, 8.1. IR (KBr): 2359, 1688, 1599, 1545, 1508, 1460, 1234, 1219, 957, 770  $\text{cm}^{-1}$ . HRMS Calcd for  $\text{C}_{18}\text{H}_{16}\text{O}_3$ :  $M^+$ , 280.1099. Found:  $m/z$  280.1103.

**(E)-4-Oxo-4-(4-propionylphenyl)but-2-enyl acetate (11):**

Pale yellow solid. TLC:  $R_f$  0.26 (hexane/ethyl acetate = 3:1). Mp. 48 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 (d,  $J$  = 8.5 Hz, 2H), 8.00 (d,  $J$  = 8.5 Hz, 2H), 7.10 – 7.01 (m, 2H), 4.87 (dd,  $J$  = 3.5, 0.5 Hz, 2H), 3.04 (q,  $J$  = 7.0 Hz, 2H), 2.17 (s, 3H), 1.25 (t,  $J$  = 7.0 Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  200.1, 189.5, 170.3, 142.1, 140.5, 139.9, 128.8, 128.2, 125.7, 63.0, 32.2, 20.8, 8.0. IR (KBr): 2980, 2940, 1726, 1688, 1668, 1624, 1281, 1252, 1223, 953, 791  $\text{cm}^{-1}$ . HRMS Calcd for  $\text{C}_{15}\text{H}_{16}\text{O}_4$ :  $M^+$ , 260.1049. Found:  $m/z$  260.1049.

**1-(4-propionylphenyl)butane-1,3-dione (12):**

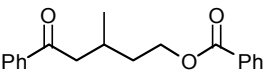
Yield: 90 %, white solid. (enol form) TLC:  $R_f$  0.47 (hexane/ethyl acetate = 3:1). Mp. 113 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (ddd,  $J$  = 8.5, 2.0, 2.0 Hz, 2H), 7.95 (ddd,  $J$  = 8.5, 2.0, 2.0 Hz, 2H), 6.22 (s, 1H), 3.04 (q,  $J$  = 7.0 Hz, 2H), 2.24 (s, 3H), 1.24 (t,  $J$  = 7.0 Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  200.0, 195.4, 180.8, 139.3, 138.3, 128.0, 127.0, 97.4, 32.0, 26.2, 8.0. IR (KBr): 3105, 2982, 1684, 1601, 1410, 1308, 1225, 955, 789  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{13}\text{H}_{14}\text{O}_3$ : C, 71.54; H, 6.47. Found: C, 71.45; H, 6.49.

**(E)-5-Oxo-5-phenylpent-3-enyl benzoate (13):**

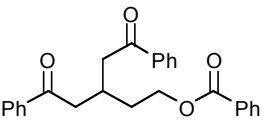
Pale yellow oil. TLC:  $R_f$  0.45 (hexane/ethyl acetate = 3:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 – 8.03 (m, 2H), 7.93 – 7.91 (m, 2H), 7.59 – 7.54 (m, 2H), 7.48 – 7.42 (m, 4H), 7.10 (dt,  $J$  = 15.5, 6.5 Hz, 1H), 7.02 (dt,  $J$  =

15.5, 1.0 Hz, 1H), 4.52 (t,  $J = 6.5$  Hz, 2H), 2.81 (qd,  $J = 6.5, 1.0$  Hz, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  190.4, 166.4, 144.3, 137.6, 133.1, 132.8, 129.9, 129.6, 128.6, 128.4, 128.3, 128.0, 62.8, 32.1. IR (neat): 3061, 2959, 1717, 1672, 1622, 1599, 1580, 1451, 1275, 1115, 972, 712  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{18}\text{H}_{16}\text{O}_3$ : C, 77.12; H, 5.75. Found: C, 76.90; H, 5.69.

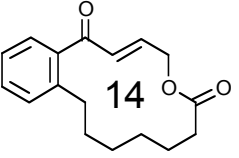
**3-Methyl-5-oxo-5-phenylpentyl benzoate (14):**

 Colorless oil. TLC:  $R_f$  0.56 (hexane/ethyl acetate = 3:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 – 8.01 (m, 2H), 7.96 – 7.94 (m, 2H), 7.58 – 7.53 (m, 2H), 7.46 – 7.41 (m, 4H), 4.43 (dt,  $J = 11.0, 6.5$  Hz, 1H), 4.38 (dt,  $J = 11.0, 6.5$  Hz, 1H), 3.05 (dd,  $J = 16.0, 6.0$  Hz, 1H), 2.88 (dd,  $J = 16.0, 7.5$  Hz, 2H), 2.50 – 2.40 (m, 1H), 1.95 – 1.85 (m, 1H), 1.77 – 1.71 (m, 1H), 1.08 (d,  $J = 6.5$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  199.6, 166.6, 137.2, 133.0, 132.9, 130.3, 129.5, 128.6, 128.3, 128.1, 63.0, 45.6, 35.5, 26.9, 20.0. IR (neat): 3063, 2961, 1715, 1682, 1599, 1582, 1451, 1275, 1113, 712  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{19}\text{H}_{20}\text{O}_3$ : C, 77.00; H, 6.80. Found: C, 76.96; H, 6.79.

**5-Oxo-3-(2-oxo-2-phenylethyl)-5-phenylpentyl benzoate (15):**

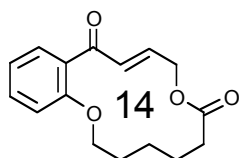
 Colorless oil. TLC:  $R_f$  0.34 (hexane/ethyl acetate = 3:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 – 7.97 (m, 4H), 7.94 – 7.92 (m, 2H), 7.57 – 7.50 (m, 3H), 7.45 – 7.42 (m, 4H), 7.38 – 7.35 (m, 2H), 4.43 (t,  $J = 6.5$  Hz, 2H), 3.26 (dd,  $J = 17.0, 6.5$  Hz, 2H), 3.15 (dd,  $J = 17.0, 6.5$  Hz, 2H), 3.00 (ttt,  $J = 6.5, 6.5, 6.5$  Hz, 1H), 2.02 (dt,  $J = 6.5, 6.5$  Hz, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  199.4, 166.5, 136.9, 133.2, 132.9, 130.1, 129.5, 128.6, 128.3, 128.1, 62.8, 42.6, 32.6, 28.4. IR (neat): 2924, 1715, 1682, 1597, 1582, 1449, 1275, 1115, 714, 691  $\text{cm}^{-1}$ . HRMS Calcd for  $\text{C}_{26}\text{H}_{24}\text{O}_4$ :  $M^+$ , 400.1675. Found:  $m/z$  400.1670.

**(E)-7,8,9,10,11,12-hexahydro-1H-benzo[f][1]oxacyclotetradecine-1,6(4H)-dione (16a):**

 Colorless oil. TLC:  $R_f$  0.47 (hexane/ethyl acetate = 3:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 (td,  $J = 7.5, 1.5$  Hz, 1H), 7.35 (dd,  $J = 7.5, 1.5$  Hz, 1H), 7.29 (d,  $J = 7.5$  Hz, 1H), 7.24 (t,  $J = 7.5$  Hz, 1H), 6.85 (dt,  $J = 15.5, 4.5$  Hz, 1H), 6.72 (dt,  $J = 15.5, 1.5$  Hz, 1H), 4.88 (dd,  $J = 4.5, 1.5$  Hz, 2H), 2.61 (t,  $J = 8.0$  Hz, 2H), 2.41 (dd,  $J = 3.0, 3.0$  Hz, 1H), 2.41 (dd,  $J = 3.0, 3.0$  Hz, 1H), 1.81 – 1.70 (m, 4H), 1.45 – 1.36 (m, 4H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  196.3, 172.7, 141.6, 139.7, 139.6, 130.7, 130.6, 129.5, 128.1, 126.0, 61.8, 34.9, 31.4, 29.2, 27.7,

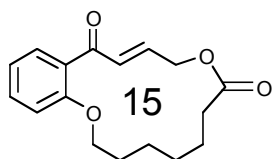
27.1, 24.3. HRMS Calcd for C<sub>17</sub>H<sub>20</sub>O<sub>3</sub>: M<sup>+</sup>, 272.1472. Found: *m/z* 272.1411.

**(*E*)-3,4,5,6-tetrahydrobenzo[*b*][1,8]dioxacyclotetradecine-7,12(2*H*,9*H*)-dione (16b):**



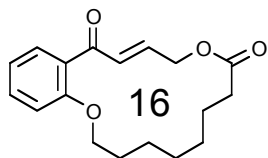
White solid. TLC: R<sub>f</sub> 0.28 (hexane/ethyl acetate = 3:1). Mp. 71 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.88 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.52 (dt, *J* = 15.5, 2.0 Hz, 1H), 7.46 (ddd, *J* = 8.5, 7.0, 2.0 Hz, 1H), 7.08 (dt, *J* = 15.5, 3.5 Hz, 1H), 7.01 (td, *J* = 8.0, 1.0 Hz, 1H), 6.93 (d, *J* = 8.5 Hz, 1H), 4.94 (dd, *J* = 3.5, 2.0 Hz, 2H), 4.12 (t, *J* = 5.0 Hz, 2H), 2.55 – 2.51 (m, 2H), 1.94 – 1.88 (m, 2H), 1.87 – 1.81 (m, 2H), 1.77 – 1.69 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 189.4, 172.6, 158.6, 139.4, 134.1, 131.9, 128.7, 127.1, 120.7, 111.9, 67.0, 61.9, 33.4, 28.0, 24.5, 24.3. IR (KBr): 2955, 2868, 1728, 1665, 1613, 1593, 1485, 1447, 1230, 1163, 1024, 966, 760 cm<sup>-1</sup>. HRMS Calcd for C<sub>17</sub>H<sub>20</sub>O<sub>3</sub>: M<sup>+</sup>, 274.1205. Found: *m/z* 274.1206.

**(*E*)-4,5,6,7-tetrahydro-2*H*-benzo[*b*][1,8]dioxacyclopentadecine-8,13(3*H*,10*H*)-dione (16c):**



Pale yellow oil. TLC: R<sub>f</sub> 0.34 (hexane/ethyl acetate = 3:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.68 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.43 (ddd, *J* = 8.5, 6.5, 2.0 Hz, 1H), 7.27 (dt, *J* = 15.0, 2.5 Hz, 1H), 7.01 (dt, *J* = 15.0, 3.0 Hz, 1H), 6.97 (td, *J* = 7.5, 1.0 Hz, 1H), 6.90 (d, *J* = 8.5 Hz, 1H), 4.88 (dd, *J* = 3.0, 2.5 Hz, 2H), 4.05 (t, *J* = 5.0 Hz, 2H), 2.50 – 2.45 (m, 2H), 1.85 – 1.74 (m, 4H), 1.65 – 1.58 (m, 2H), 1.51 – 1.43 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 190.9, 172.8, 158.0, 137.8, 133.4, 131.2, 128.5, 128.4, 120.4, 111.5, 67.6, 62.0, 32.6, 29.2, 27.4, 25.1, 24.5. IR (neat): 2931, 1738, 1668, 1622, 1597, 1485, 1450, 1238, 1151, 968, 758 cm<sup>-1</sup>. HRMS Calcd for C<sub>17</sub>H<sub>20</sub>O<sub>3</sub>: M<sup>+</sup>, 288.1362. Found: *m/z* 288.1365.

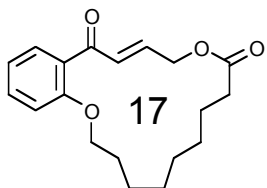
**(*E*)-3,4,5,6,7,8-hexahydrobenzo[*b*][1,8]dioxacyclohexadecine-9,14(2*H*,11*H*)-dione (16d):**



Colorless oil. TLC: R<sub>f</sub> 0.41 (hexane/ethyl acetate = 3:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.68 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.45 (ddd, *J* = 9.0, 7.0, 2.0 Hz, 1H), 7.21 (dt, *J* = 15.0, 2.0 Hz, 1H), 7.01 (td, *J* = 8.0, 1.0 Hz, 1H), 6.97 (dt, *J* = 15.0, 4.5 Hz, 1H), 6.97 (d, *J* = 7.0 Hz, 1H), 4.80 (dd, *J* = 4.0, 2.0 Hz, 2H), 4.10 (t, *J* = 5.5 Hz, 2H), 2.46 – 2.42 (m, 2H), 1.84 – 1.73 (m, 4H), 1.47 – 1.41 (m, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 191.9, 173.2, 158.1, 137.4, 133.5,

131.0, 130.5, 128.8, 120.8, 112.5, 68.3, 63.0, 34.0, 28.6, 27.3, 26.6, 25.6, 23.8. IR (neat): 2930, 1732, 1668, 1622, 1597, 1450, 1290, 1242, 1155, 964, 756  $\text{cm}^{-1}$ . HRMS Calcd for  $\text{C}_{17}\text{H}_{20}\text{O}_3$ :  $\text{M}^+$ , 302.1518. Found:  $m/z$  302.1521.

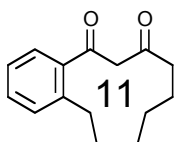
**(E)-4,5,6,7,8,9-hexahydro-2H-benzo[b][1,8]dioxacycloheptadecine-10,15(3H,12H)-dione (16e):**



Colorless oil. TLC:  $R_f$  0.44 (hexane/ethyl acetate = 3:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 (dd,  $J = 7.5, 2.0$  Hz, 1H), 7.43 (ddd,  $J = 8.5, 7.5, 2.0$  Hz, 1H), 7.02 – 6.90 (m, 4H), 4.77 (dd,  $J = 4.5, 1.5$  Hz, 2H), 4.04 (t,  $J = 5.5$  Hz, 2H), 2.44 – 2.38 (m, 2H), 1.80 – 1.73 (m, 2H), 1.73 – 1.66 (m, 2H), 1.52 – 1.44 (m, 2H), 1.43 – 1.33 (m, 6H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  193.0, 173.4, 157.7, 137.3, 133.0, 131.2, 130.1, 129.5, 120.5, 112.0, 68.1, 63.0, 34.2, 29.0, 27.2, 27.1, 26.7, 24.9, 24.3. IR (neat): 2934, 1736, 1672, 1626, 1597, 1451, 1290, 1244, 1147, 1028, 756  $\text{cm}^{-1}$ . HRMS Calcd for  $\text{C}_{17}\text{H}_{20}\text{O}_3$ :  $\text{M}^+$ , 316.1675. Found:  $m/z$  316.1677.

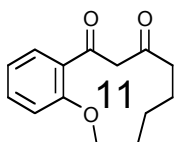
**8,9,10,11,12,13-hexahydro-5H-benzo[11]annulene-5,7(6H)-dione (17a):**



Yield: 78 %, white solid. (keto form) TLC:  $R_f$  0.37 (hexane/ethyl acetate = 3:1). Mp. 76  $^{\circ}\text{C}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 (d,  $J = 8.0$  Hz, 1H), 7.44 (td,  $J = 7.5, 1.5$  Hz, 1H), 7.32 – 7.28 (m, 2H), 4.19 (s, 2H), 2.99 (t,  $J = 6.0$  Hz, 2H), 2.54 (t,  $J = 6.0$  Hz, 2H), 1.63 – 1.57 (m, 4H), 1.16 – 1.10 (m, 2H), 0.99 – 0.94 (m, 2H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  203.7, 196.1, 142.4, 140.0, 131.9, 131.5, 127.9, 125.6, 61.6, 40.7, 30.1, 27.8, 25.9, 23.9, 23.8. IR (KBr): 2959, 2932, 2853, 1717, 1670, 1597, 1568, 1416, 1250, 984, 754  $\text{cm}^{-1}$ . HRMS Calcd for  $\text{C}_{15}\text{H}_{18}\text{O}_2$ :  $\text{M}^+$ , 230.1307. Found:  $m/z$  230.1312.

**3,4,5,6-tetrahydrobenzo[b][1]oxacycloundecine-7,9(2H,8H)-dione (17b):**

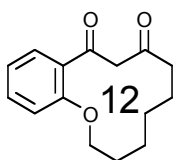


Yield: 73 %, white solid. (keto form) TLC:  $R_f$  0.24 (hexane/ethyl acetate = 3:1). Mp. 110  $^{\circ}\text{C}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (dd,  $J = 8.0, 1.5$  Hz, 1H), 7.46 (ddd,  $J = 8.0, 6.5, 1.5$  Hz, 1H), 6.99 (ddd,  $J = 7.5, 6.5, 1.0$  Hz, 1H), 6.88 (d,  $J = 8.0$  Hz, 1H), 4.05 (t,  $J = 5.0$  Hz, 2H), 3.99 (s, 2H), 2.65 – 2.60 (m, 2H), 1.98 – 1.87 (m, 4H), 1.75 – 1.68 (m, 2H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  204.5, 193.6, 158.6, 134.5, 130.8, 126.6, 120.7, 112.0, 70.5, 57.4, 41.5, 25.6, 25.2, 23.2. IR (KBr): 2945,

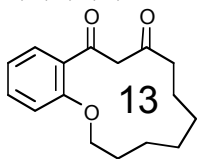
2874, 1709, 1672, 1595, 1574, 1451, 1310, 1230, 1036, 762  $\text{cm}^{-1}$ . HRMS Calcd for  $\text{C}_{15}\text{H}_{18}\text{O}_2$ :  $M^+$ , 232.1099. Found:  $m/z$  232.1095.

**4,5,6,7-tetrahydro-2*H*-benzo[*b*][1]oxacyclododecine-8,10(3*H*,9*H*)-dione (17c):**



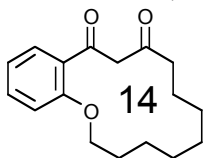
Yield: 61 %, white solid. (keto form) TLC:  $R_f$  0.41 (hexane/ethyl acetate = 3:1). Mp. 86 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (dd,  $J$  = 8.0, 1.5 Hz, 1H), 7.46 (ddd,  $J$  = 8.5, 7.5, 2.0 Hz, 1H), 7.01 (td,  $J$  = 7.5, 1.0 Hz, 1H), 6.90 (d,  $J$  = 8.0 Hz, 1H), 4.26 (s, 2H), 4.07 (t,  $J$  = 5.0 Hz, 2H), 2.50 (dd,  $J$  = 3.0, 3.0 Hz, 1H), 2.49 (dd,  $J$  = 3.0, 3.0 Hz, 1H), 1.94 – 1.87 (m, 4H), 1.65 – 1.59 (m, 2H), 1.56 – 1.48 (m, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  206.0, 194.7, 158.5, 134.6, 131.4, 126.4, 120.7, 112.1, 69.0, 57.1, 42.5, 25.8, 25.7, 24.9, 21.8. IR (KBr): 2943, 2855, 1713, 1663, 1597, 1574, 1487, 1451, 1306, 1234, 976, 760  $\text{cm}^{-1}$ . HRMS Calcd for  $\text{C}_{15}\text{H}_{18}\text{O}_2$ :  $M^+$ , 246.1256. Found:  $m/z$  246.1258.

**3,4,5,6,7,8-hexahydrobenzo[*b*][1]oxacyclotridecine-9,11(2*H*,10*H*)-dione (17d):**



Yield: 61 %, white solid. (enol form) TLC:  $R_f$  0.56 (hexane/ethyl acetate = 3:1). Mp. 107 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (dd,  $J$  = 8.0, 1.5 Hz, 1H), 7.41 (ddd,  $J$  = 8.5, 7.5, 2.0 Hz, 1H), 7.01 (td,  $J$  = 7.5, 1.0 Hz, 1H), 6.88 (d,  $J$  = 8.5 Hz, 1H), 6.70 (s, 1H), 4.00 (t,  $J$  = 5.0 Hz, 2H), 2.47 – 2.40 (m, 2H), 1.87 – 1.80 (m, 2H), 1.72 – 1.63 (m, 4H), 1.58 – 1.51 (m, 2H), 1.49 – 1.42 (m, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  192.6, 184.9, 158.1, 133.0, 130.1, 125.3, 120.4, 111.9, 100.8, 68.9, 36.2, 27.8, 27.3, 25.4, 24.0, 23.2. IR (KBr): 2938, 2849, 1605, 1576, 1489, 1464, 1406, 1252, 1005, 959, 775  $\text{cm}^{-1}$ . HRMS Calcd for  $\text{C}_{15}\text{H}_{18}\text{O}_2$ :  $M^+$ , 260.1412. Found:  $m/z$  260.1412.

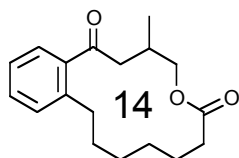
**4,5,6,7,8,9-hexahydro-2*H*-benzo[*b*][1]oxacyclotetradecine-10,12(3*H*,11*H*)-dione (17e):**



Yield: 81 %, white solid. (enol form) TLC:  $R_f$  0.65 (hexane/ethyl acetate = 3:1). Mp. 96 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (dd,  $J$  = 8.0, 1.5 Hz, 1H), 7.42 (ddd,  $J$  = 8.0, 7.0, 2.0 Hz, 1H), 7.02 (ddd,  $J$  = 7.5, 7.0, 1.0 Hz, 1H), 6.90 (dd,  $J$  = 8.5, 1.0 Hz, 1H), 6.67 (s, 1H), 4.04 (t,  $J$  = 5.0 Hz, 2H), 2.43 (dd,  $J$  = 3.0, 3.0 Hz, 1H), 2.42 (dd,  $J$  = 3.0, 3.0 Hz, 1H), 1.88 – 1.81 (m, 2H), 1.78 – 1.71 (m, 2H), 1.66 – 1.58 (m, 2H), 1.51 – 1.43 (m, 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  194.9, 183.1, 158.1, 133.1, 130.5, 124.3, 120.4, 111.7, 102.6, 68.0, 36.6, 28.0, 26.5, 24.9,

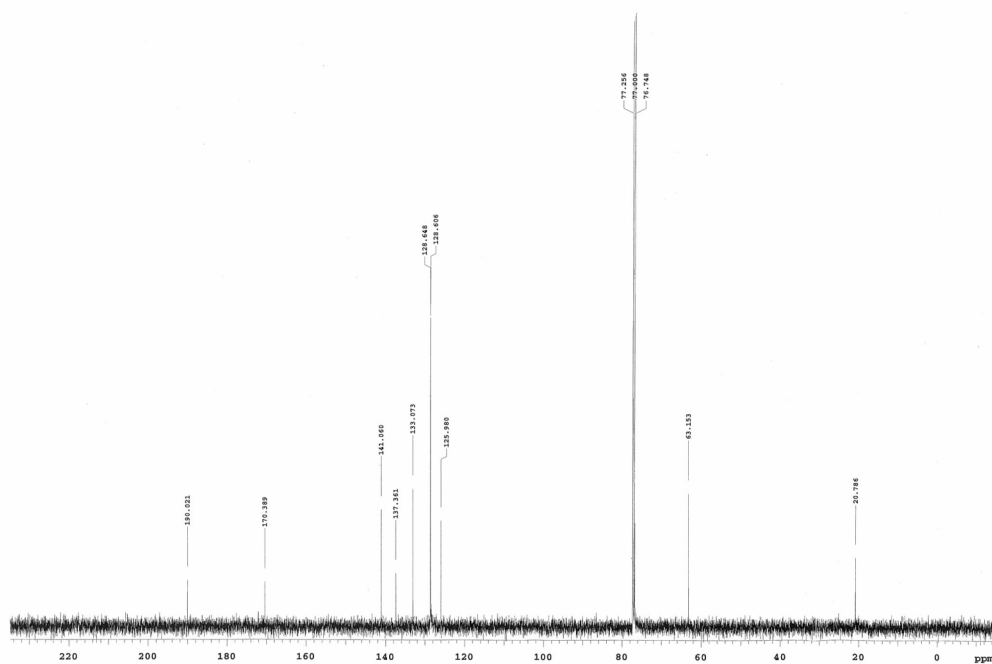
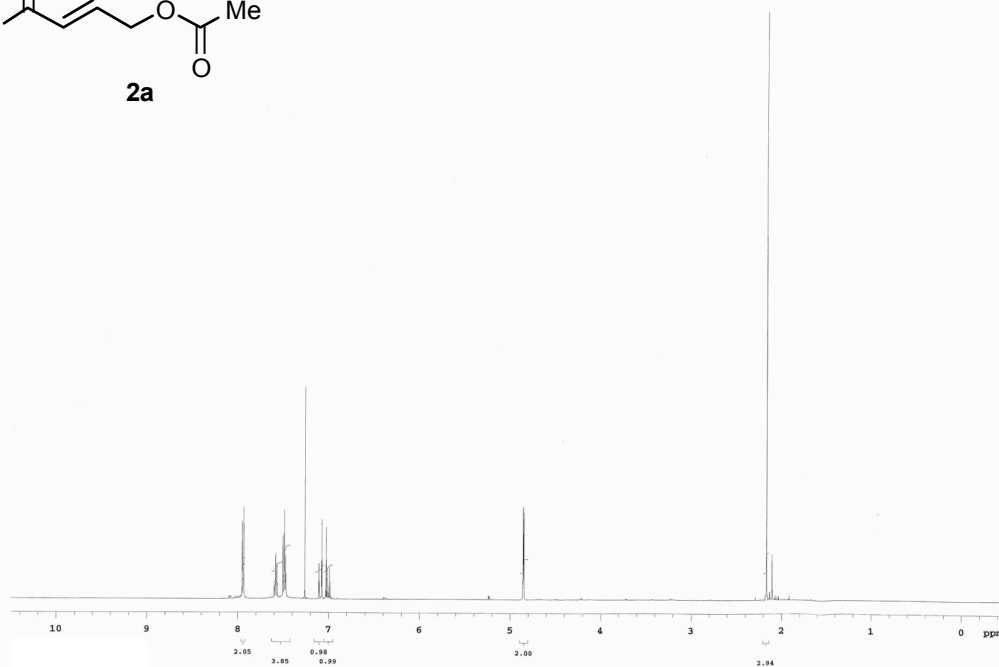
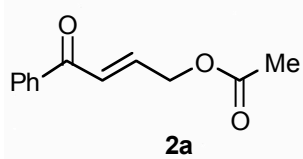
24.7, 24.3, 22.8. IR (KBr): 2936, 2853, 1603, 1580, 1491, 1445, 1252, 1074, 972, 754  $\text{cm}^{-1}$ . HRMS Calcd for  $\text{C}_{15}\text{H}_{18}\text{O}_2$ :  $M^+$ , 274.1569. Found:  $m/z$  274.1569.

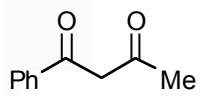
**3-Methyl-3,4,7,8,9,10,11,12-octahydro-1*H*-benzo[*f*][1]oxacyclotetradecine-1,6(2*H*)-dione (18):**



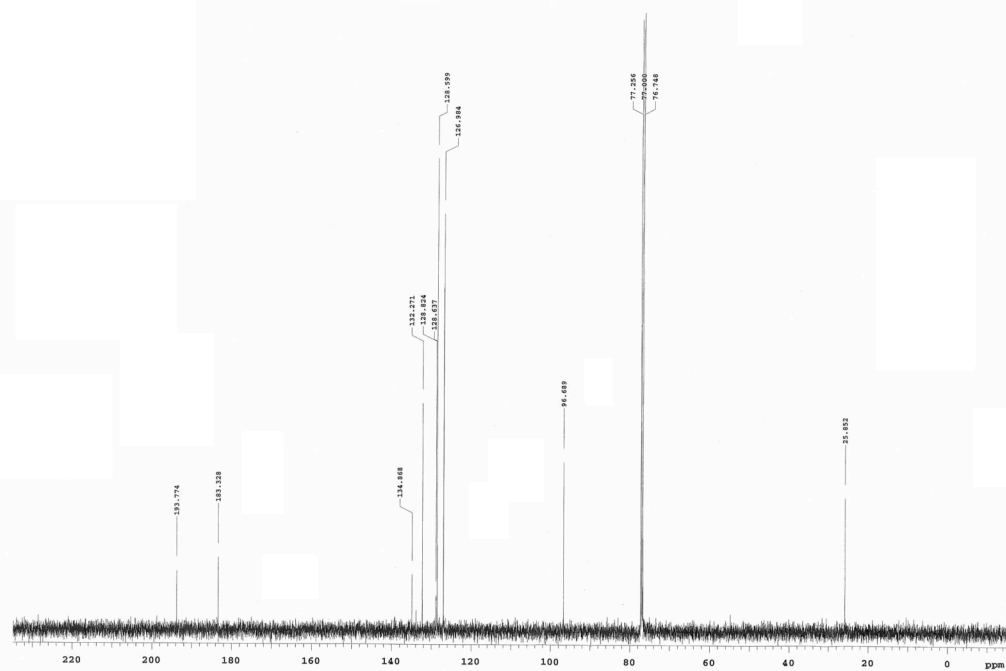
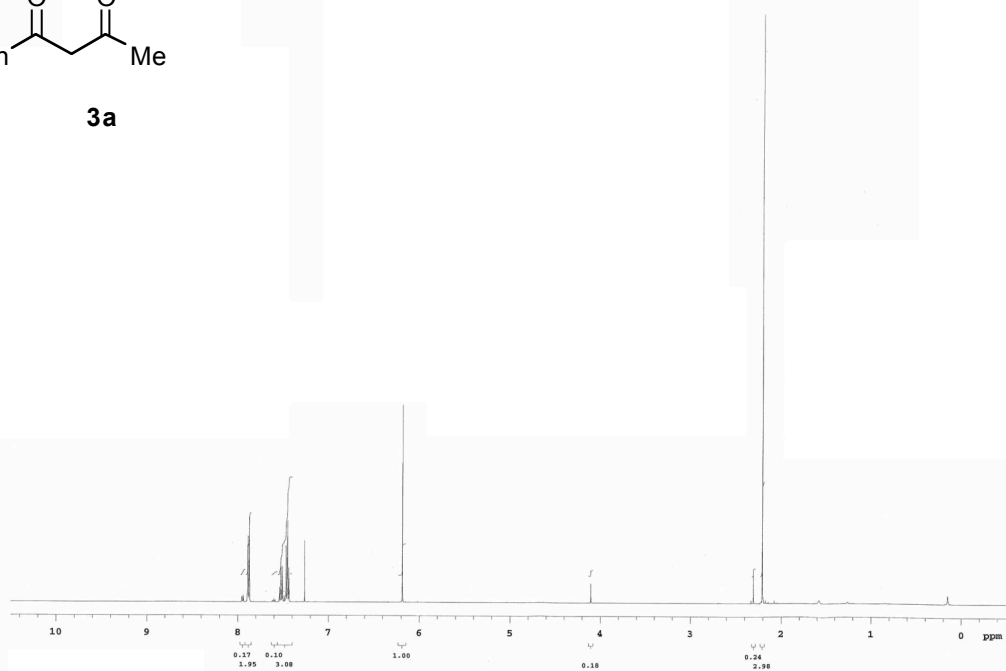
White solid. TLC:  $R_f$  0.56 (hexane/ethyl acetate = 3:1). Mp. 95 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 (td,  $J = 7.0, 1.5$  Hz, 1H), 7.30 – 7.25 (m, 2H), 7.21 (td,  $J = 7.5, 1.5$  Hz, 1H), 4.37 (dd,  $J = 11.0, 7.0$  Hz, 1H), 3.91 (dd,  $J = 11.0, 7.5$  Hz, 1H), 3.03 (dd,  $J = 19.0, 6.5$  Hz, 1H), 2.84 (dd,  $J = 19.0, 6.0$  Hz, 1H), 2.76 (dt,  $J = 14.0, 8.0$  Hz, 1H), 2.65 – 2.56 (m, 2H), 2.41 (ddd,  $J = 14.5, 7.0, 4.0$  Hz, 1H), 2.28 (ddd,  $J = 14.5, 9.5, 4.5$  Hz, 1H), 1.67 – 1.57 (m, 4H), 1.32 – 1.22 (m, 4H), 1.09 (d,  $J = 7.0$  Hz 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  206.0, 173.6, 141.4, 139.6, 130.2, 130.1, 125.9, 125.5, 67.6, 46.4, 34.9, 30.4, 30.2, 27.9, 27.1, 26.9, 24.4, 17.5. IR (KBr): 3055, 2926, 2855, 1728, 1684, 1597, 1570, 1370, 1256, 1130, 750  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{18}\text{H}_{24}\text{O}_3$ : C, 74.97; H, 8.39. Found: C, 74.74; H, 8.43.

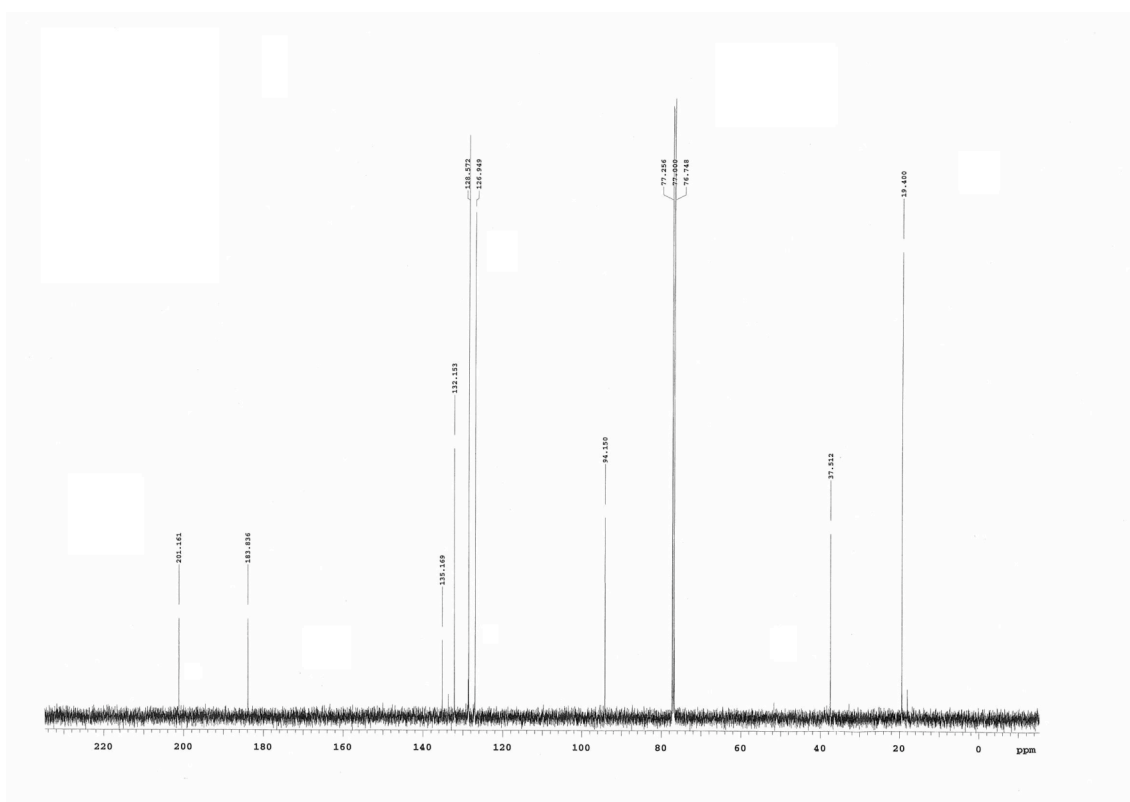
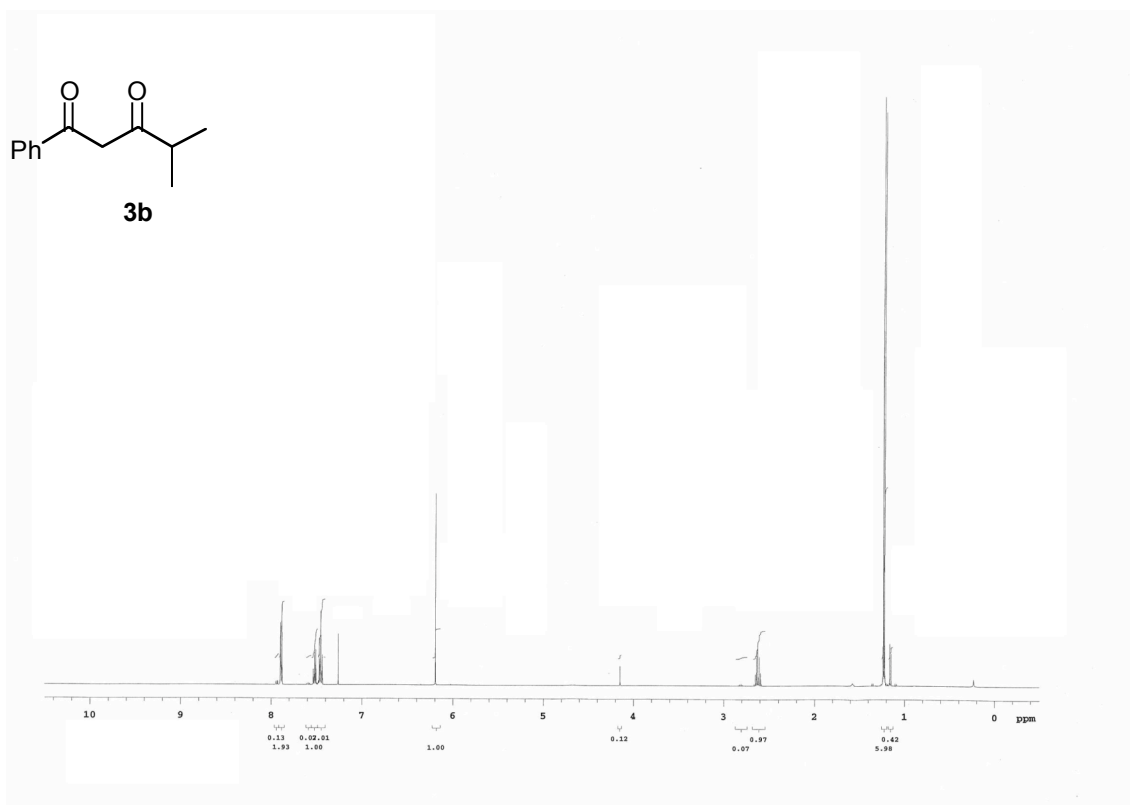
# $^1\text{H}$ NMR and $^{13}\text{C}$ NMR Spectra of the Substrates and the Products

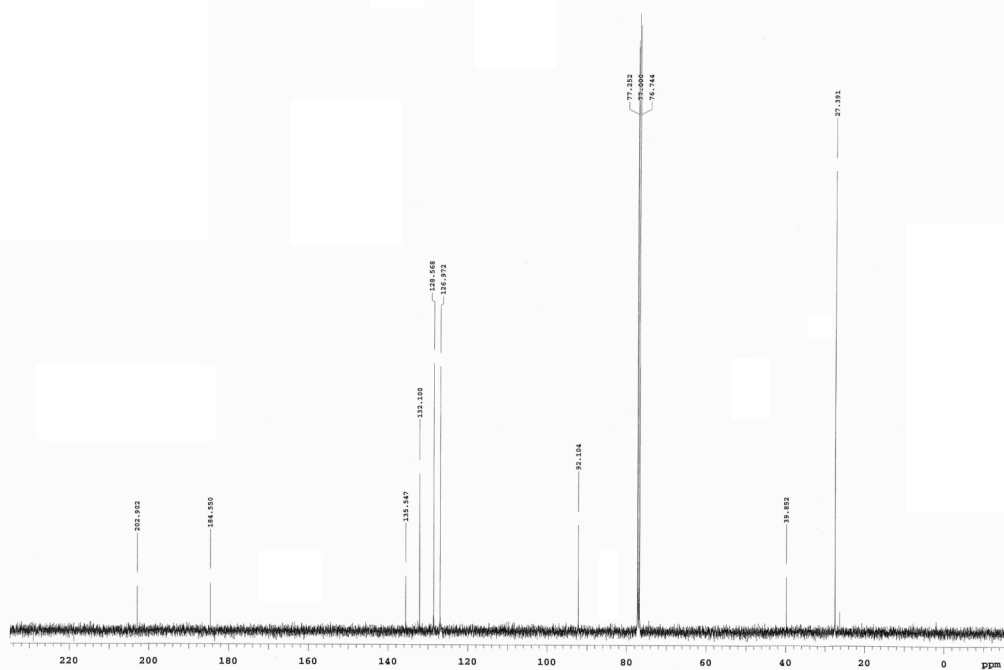
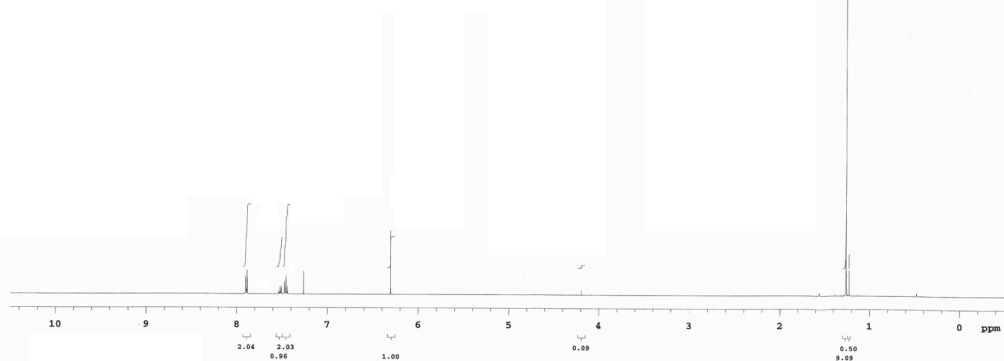
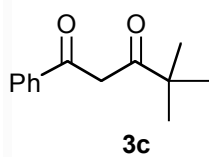


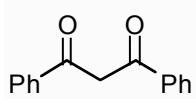


**3a**

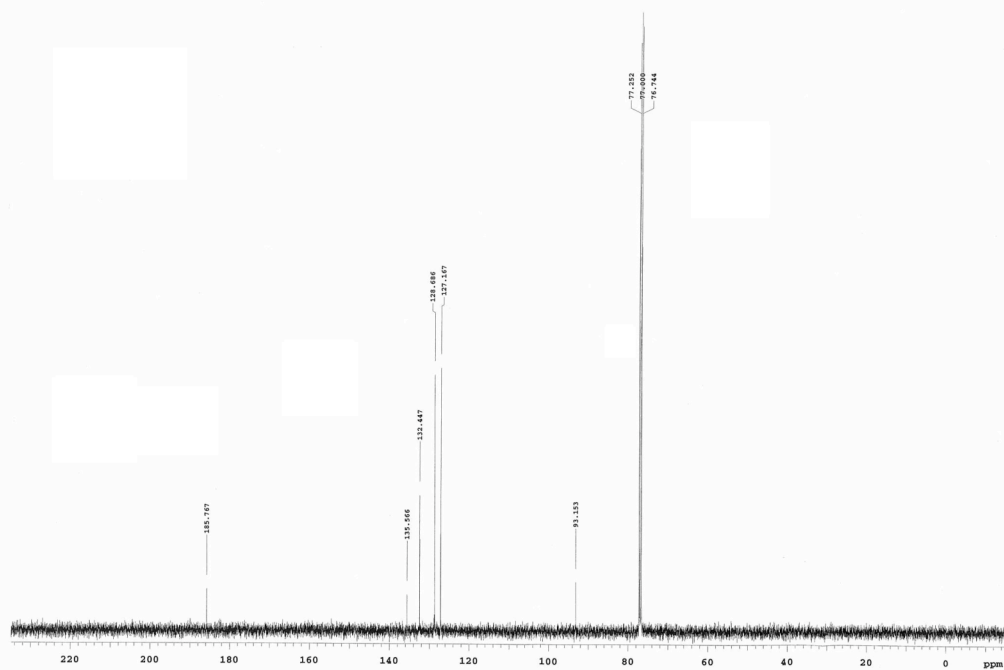
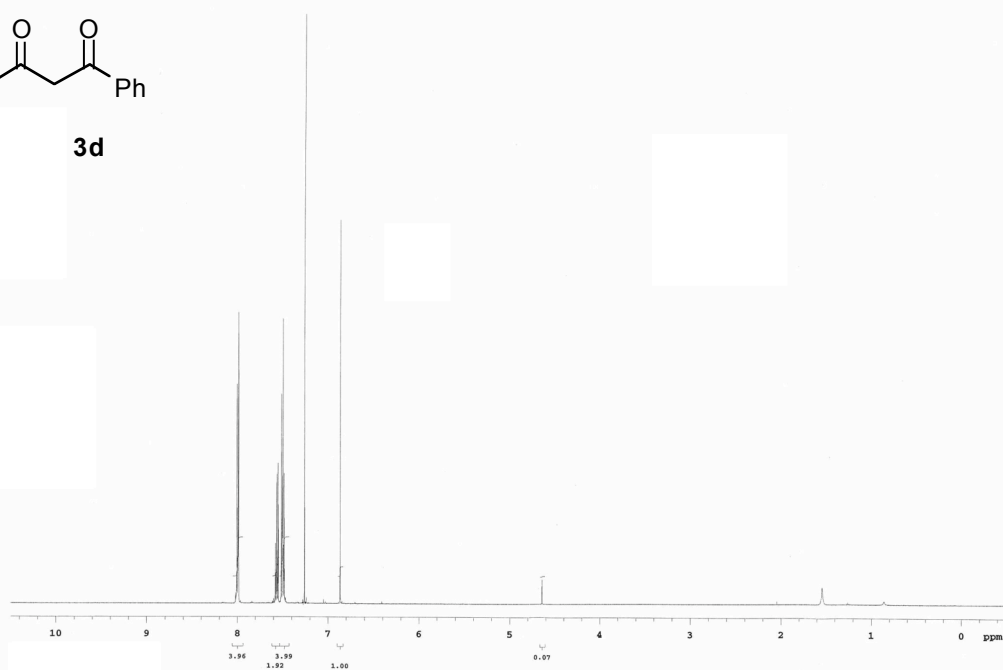


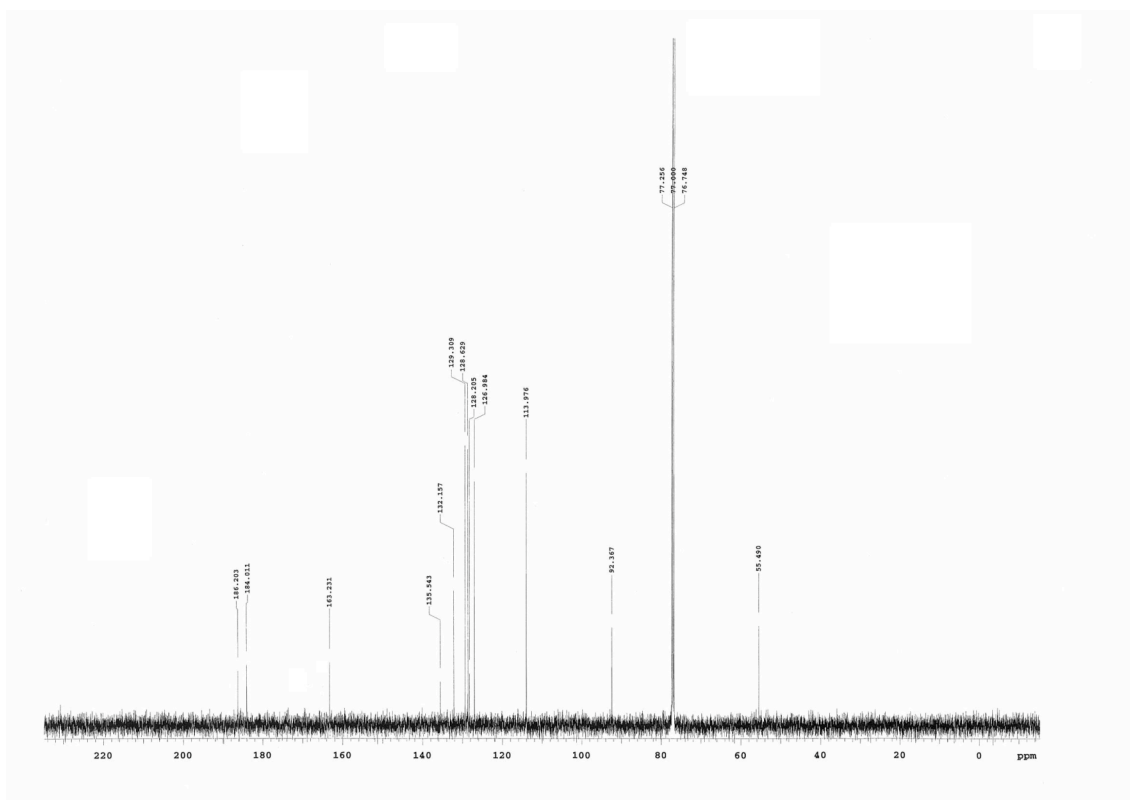
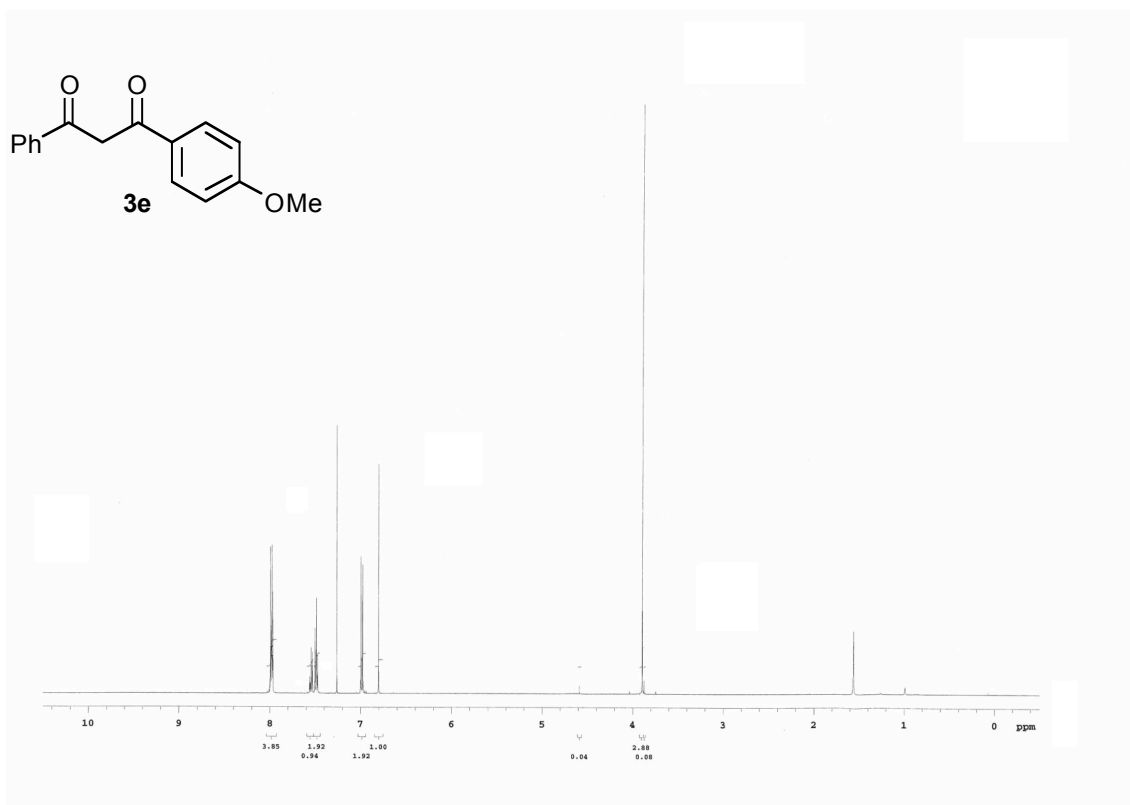


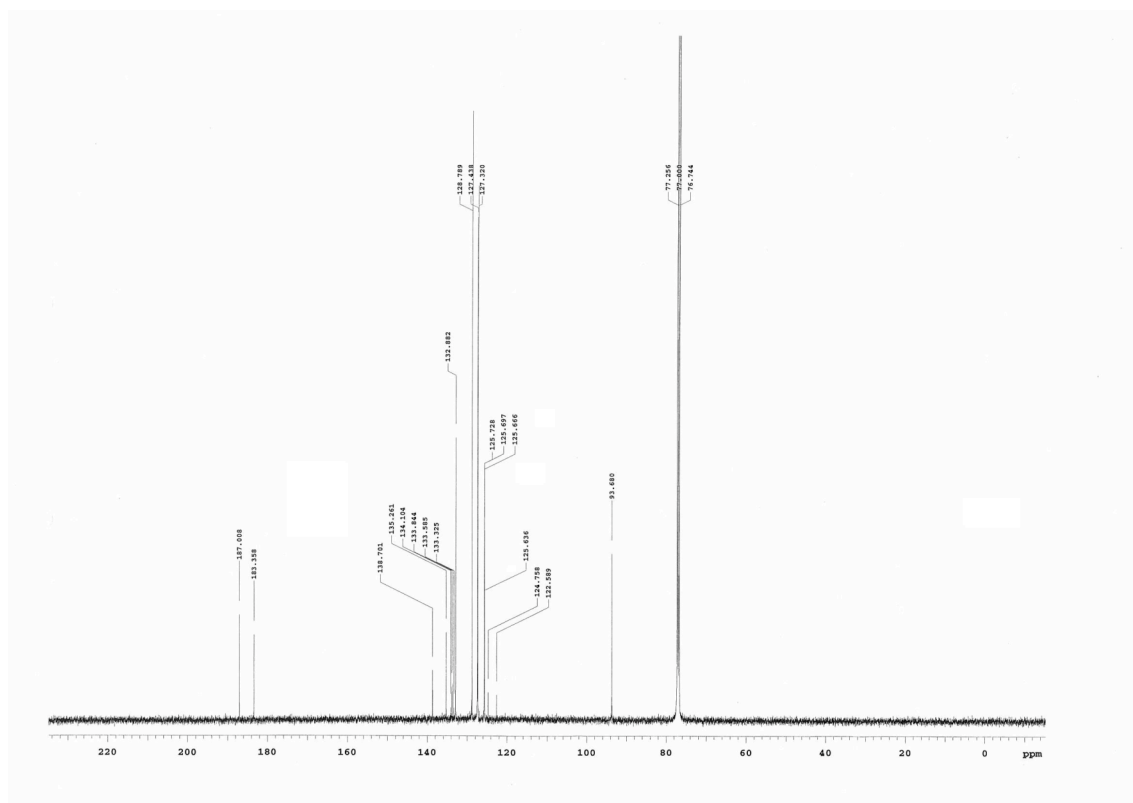
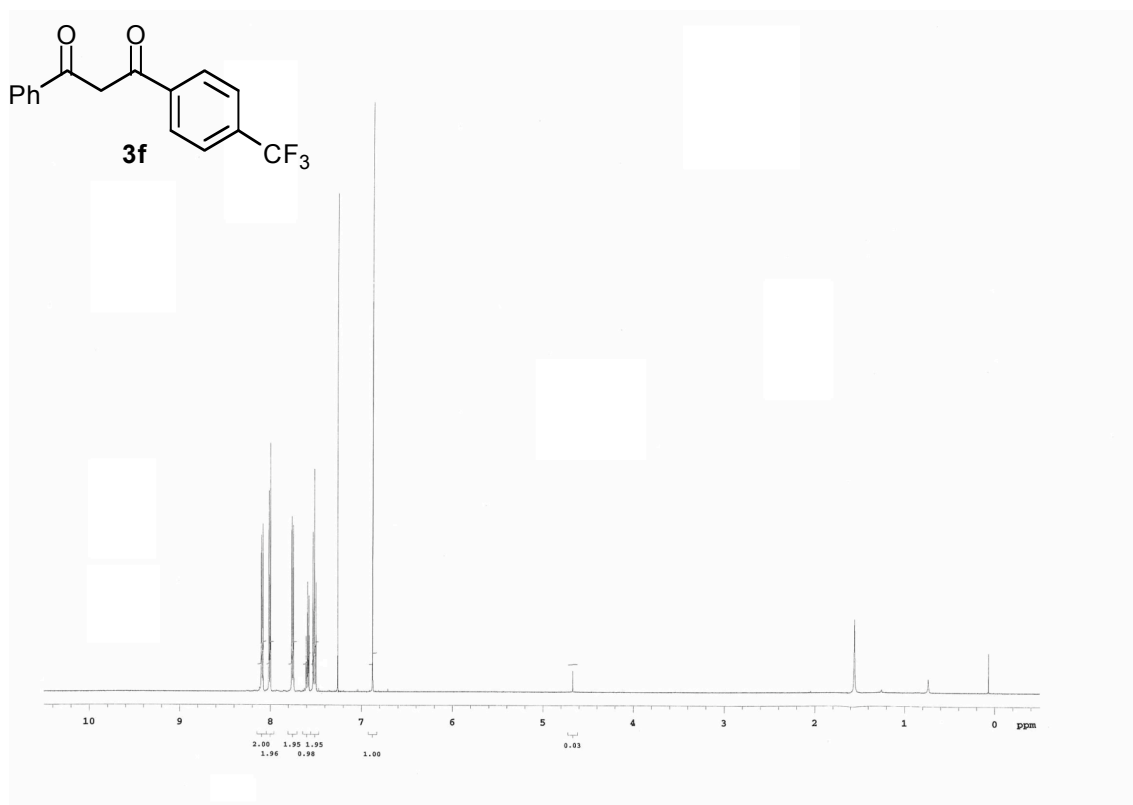


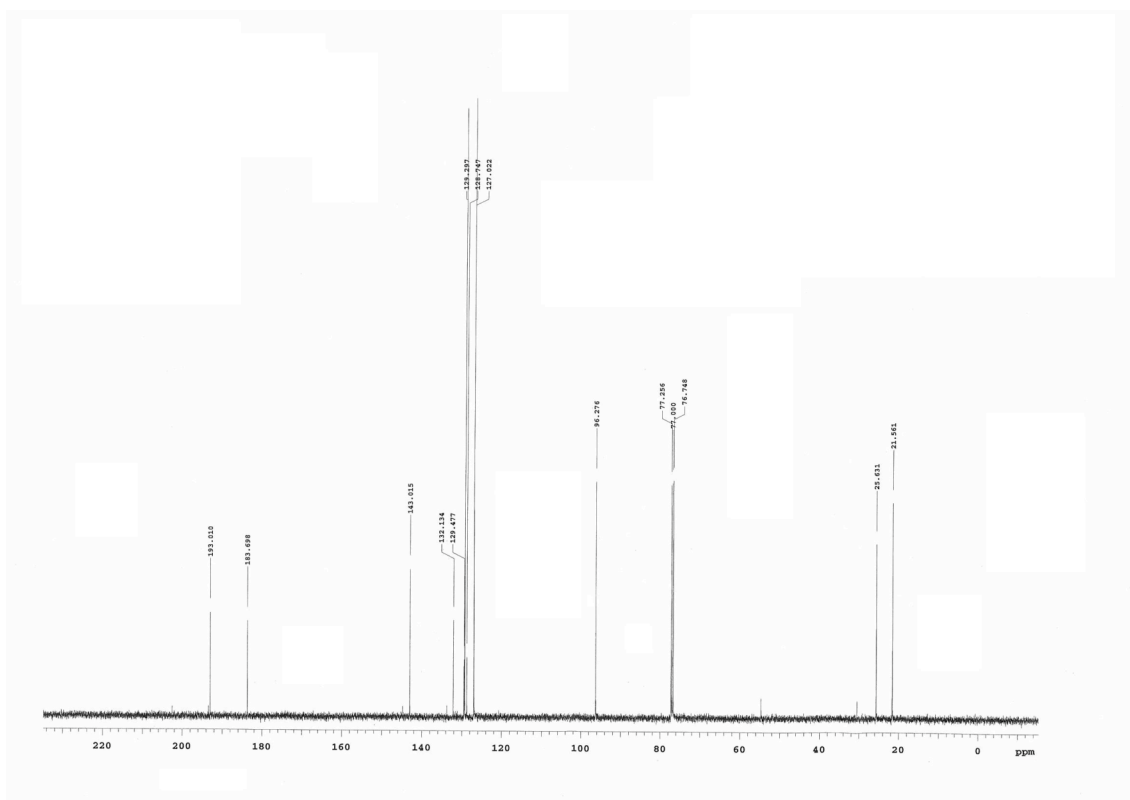
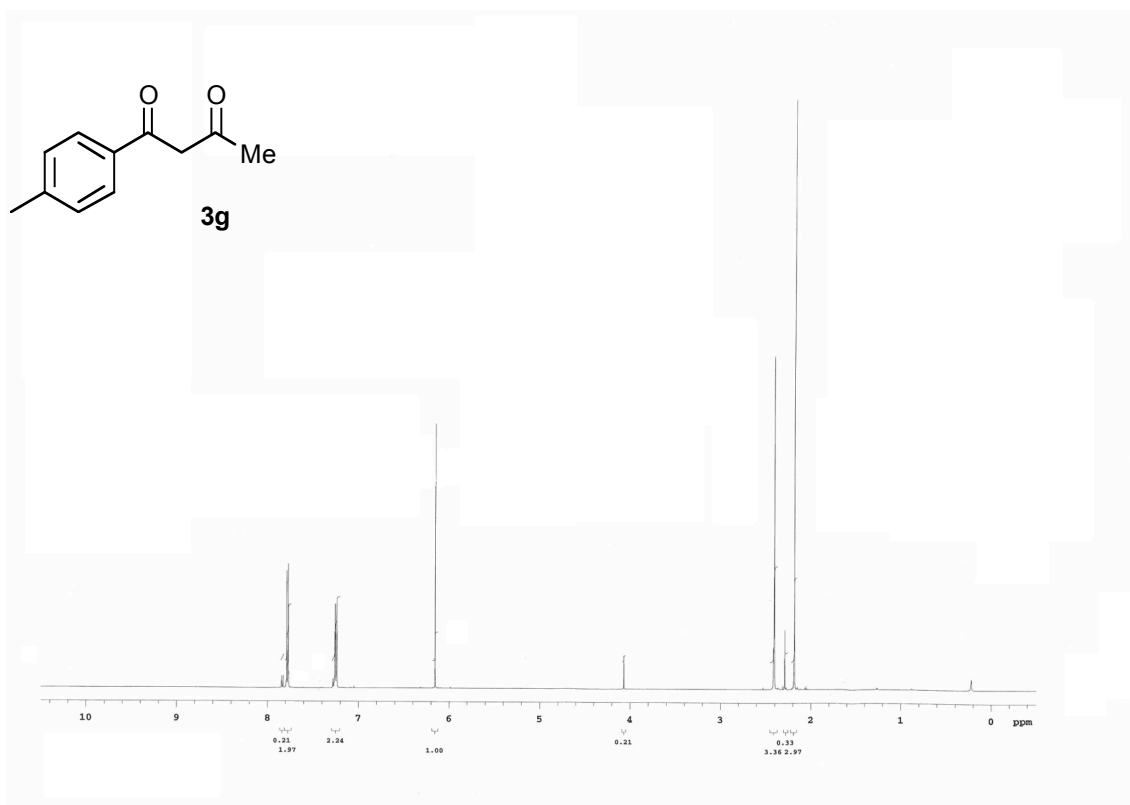


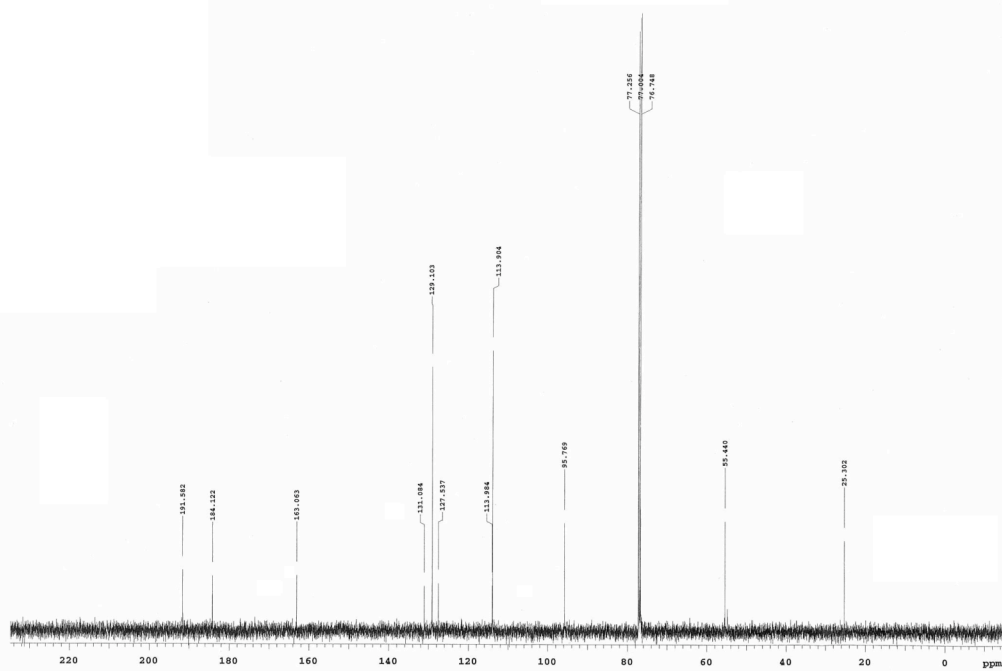
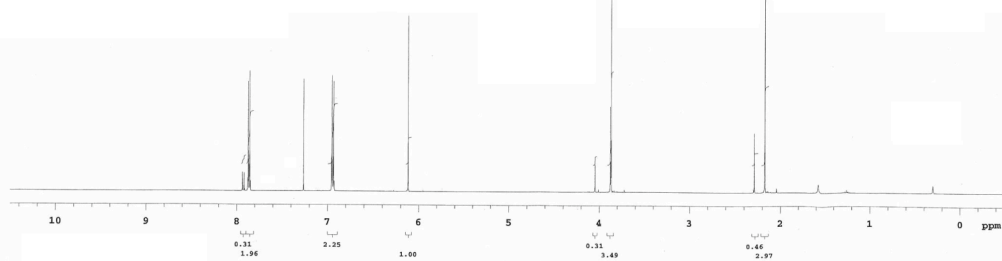
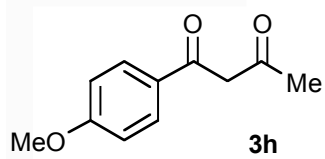
**3d**

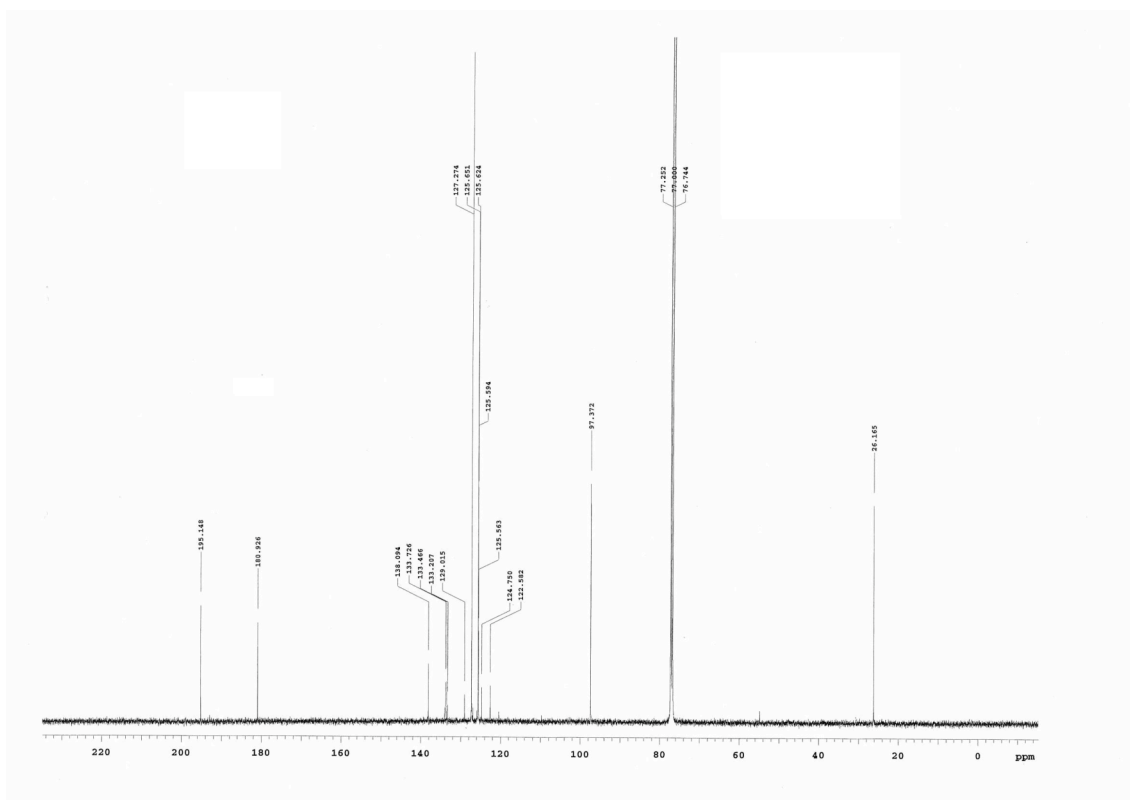
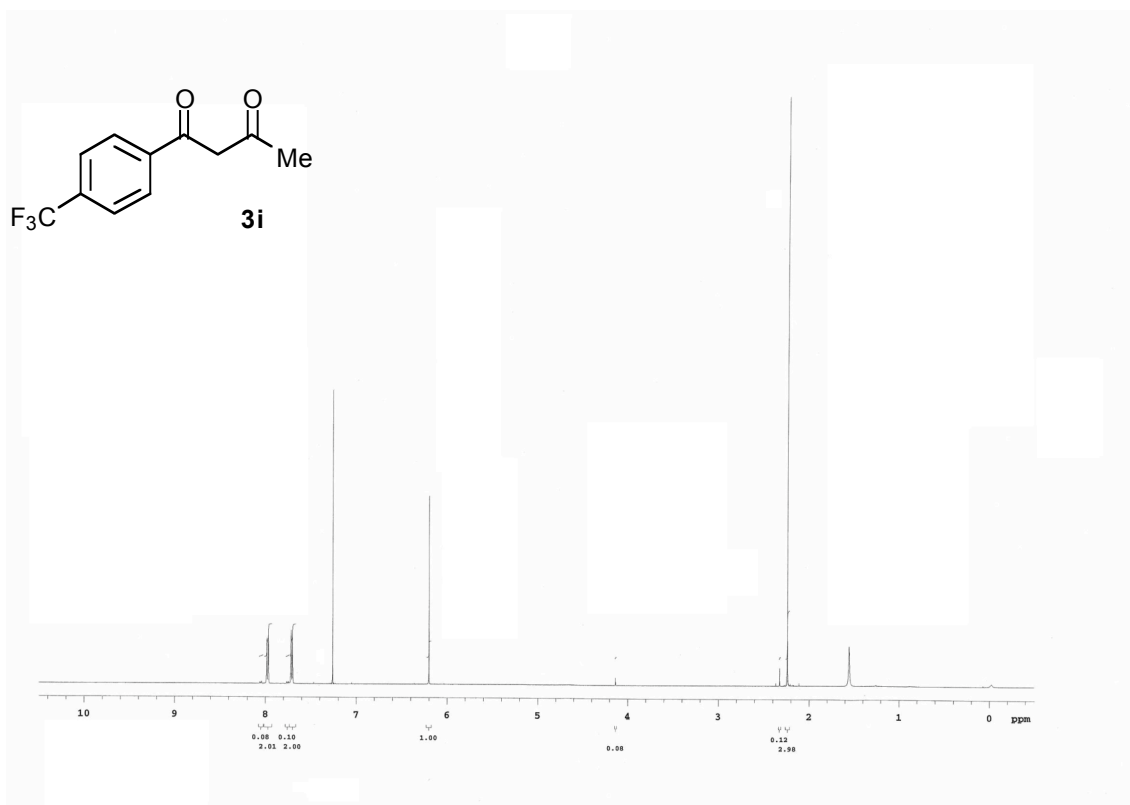


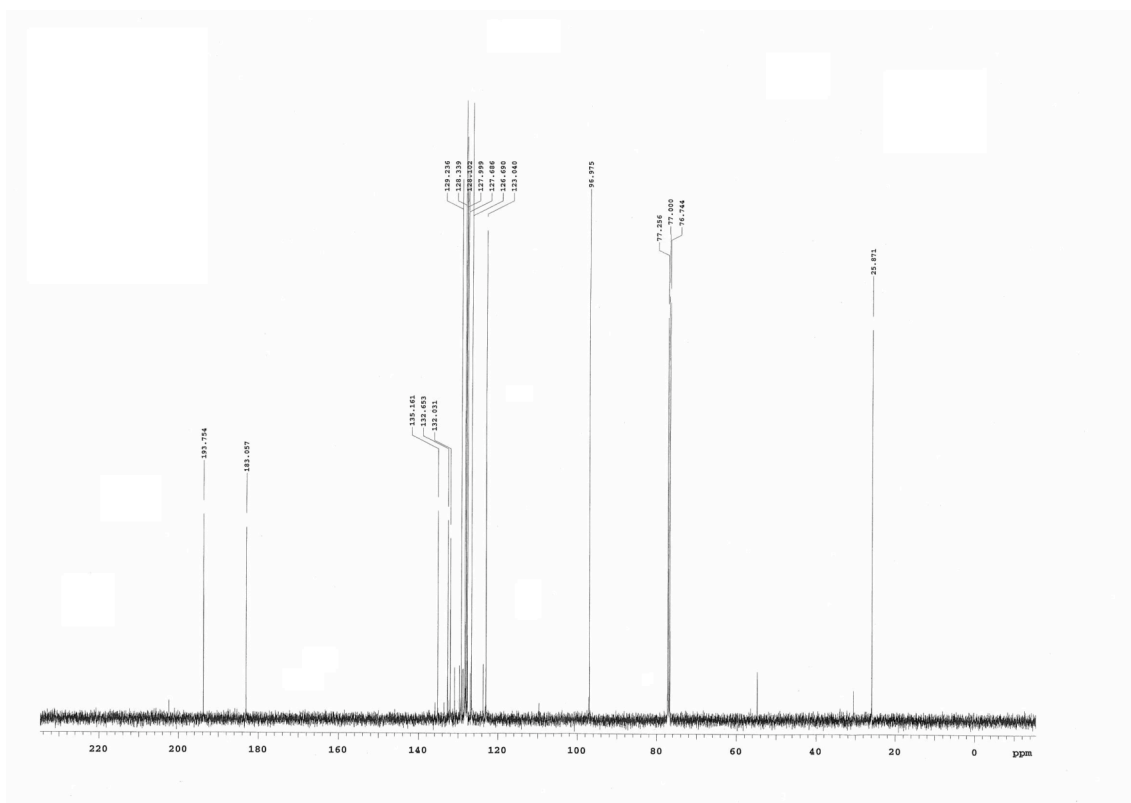
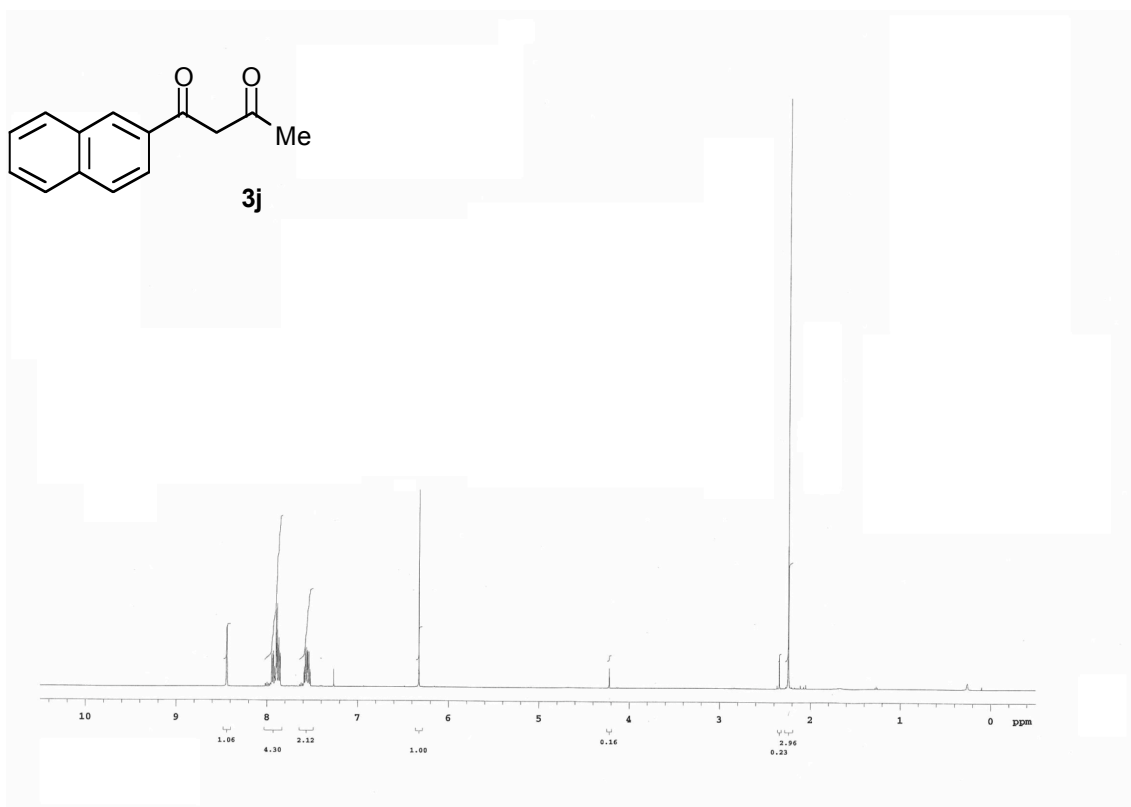


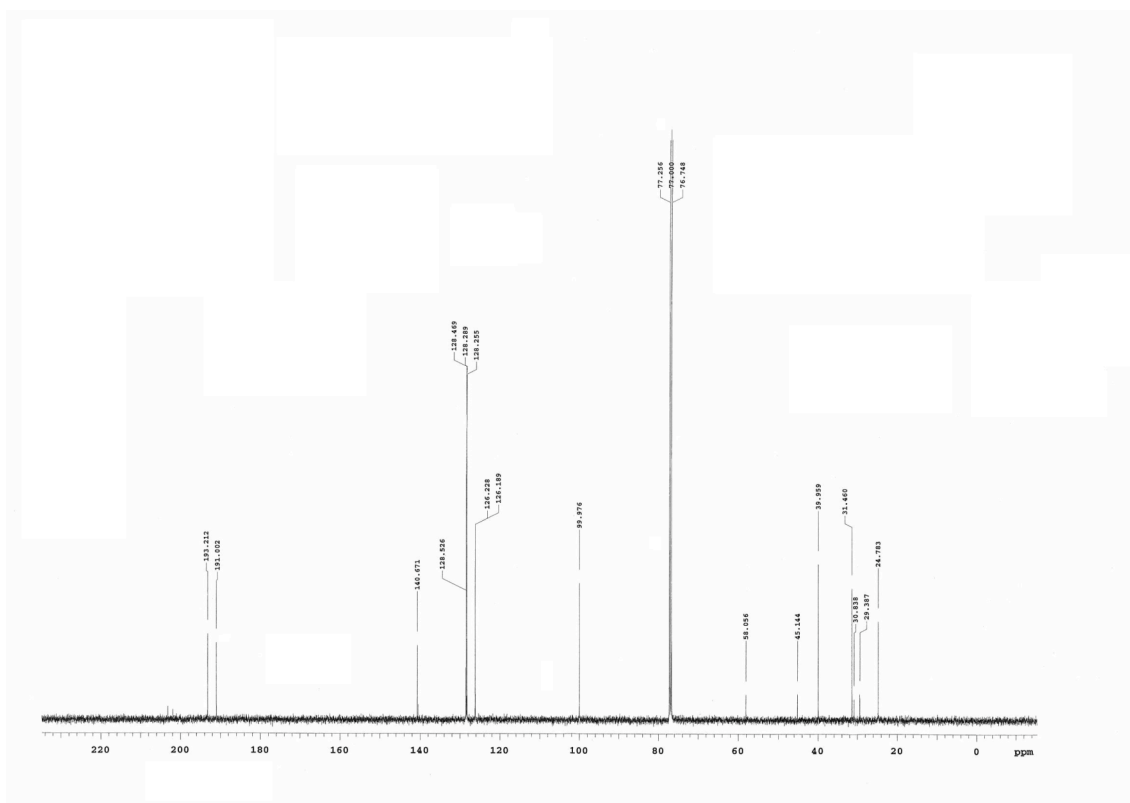
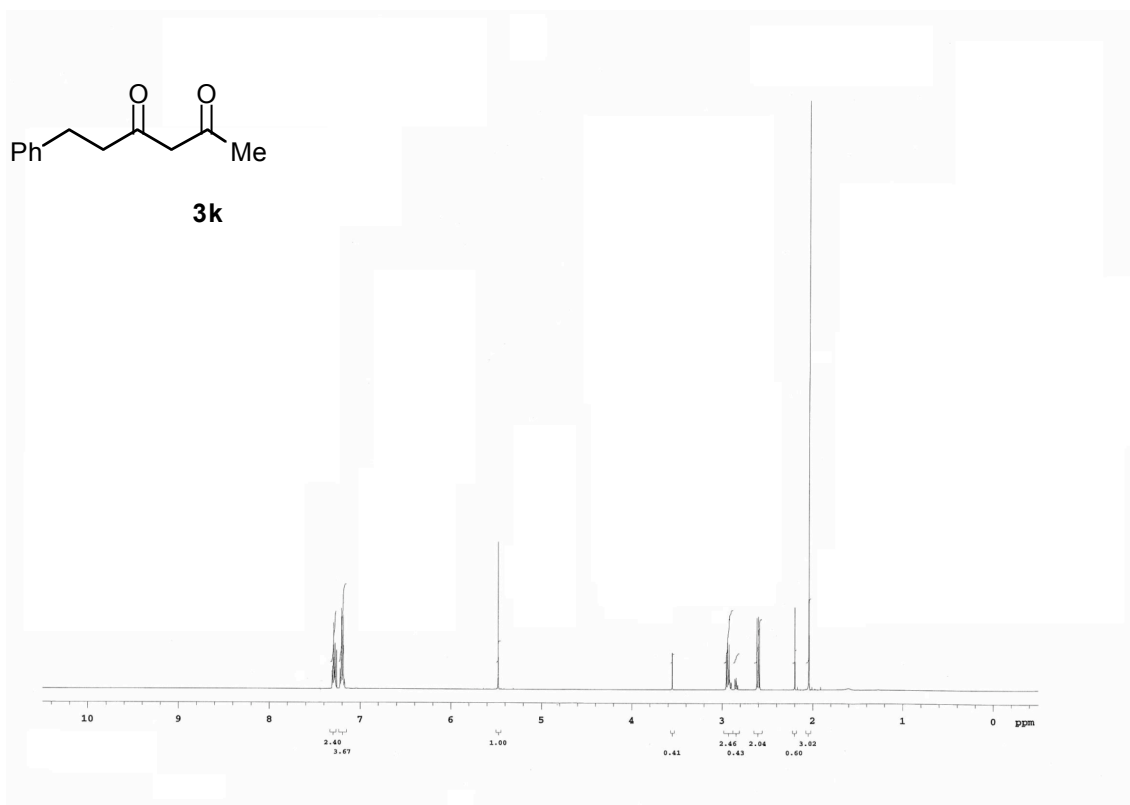


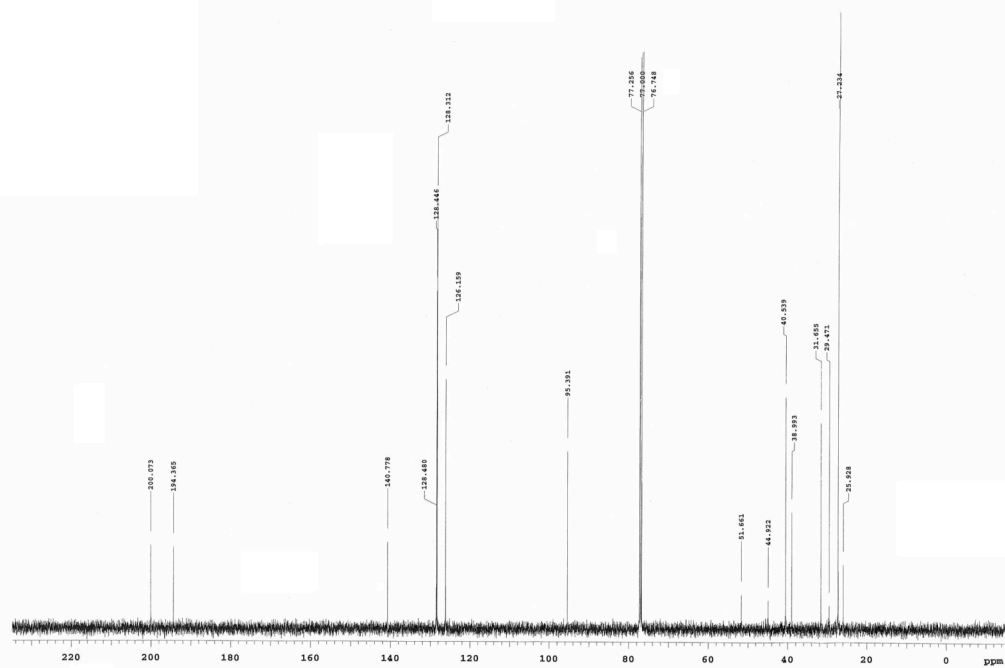
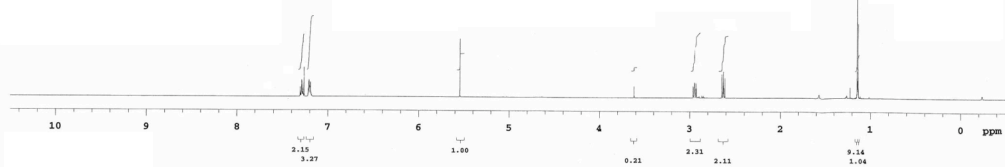
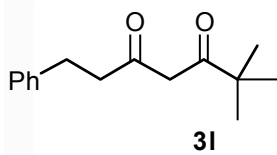


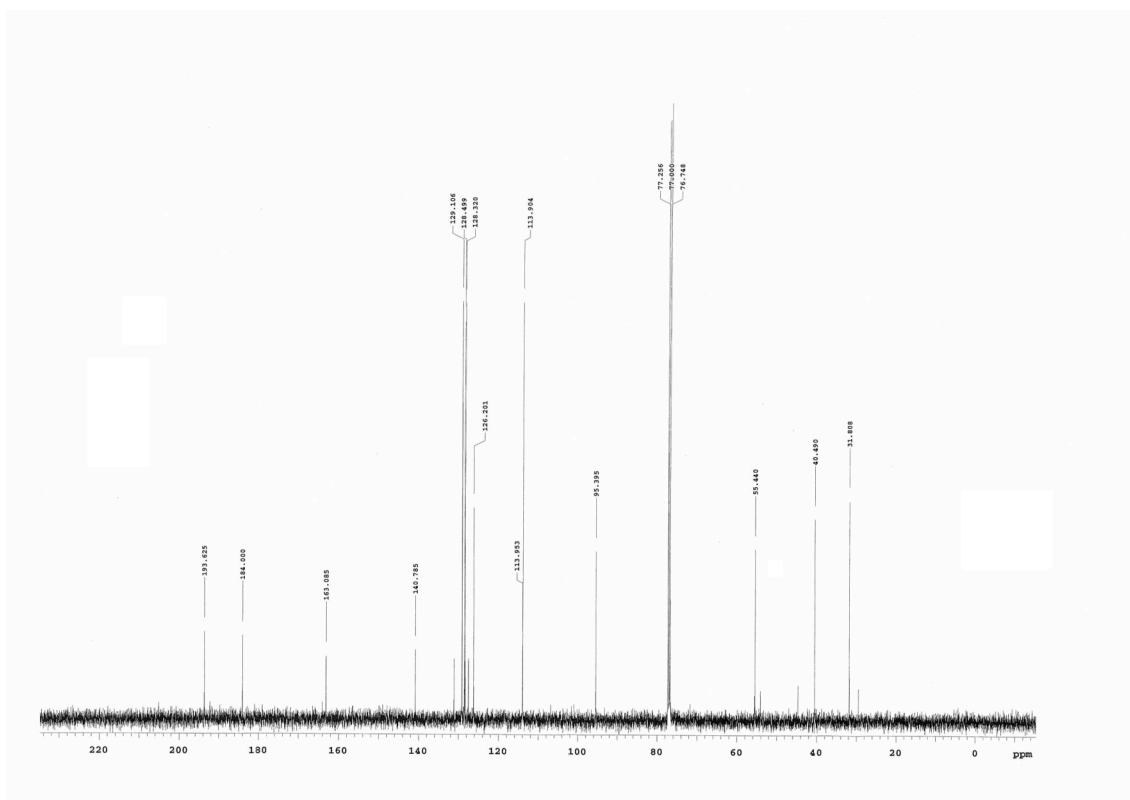
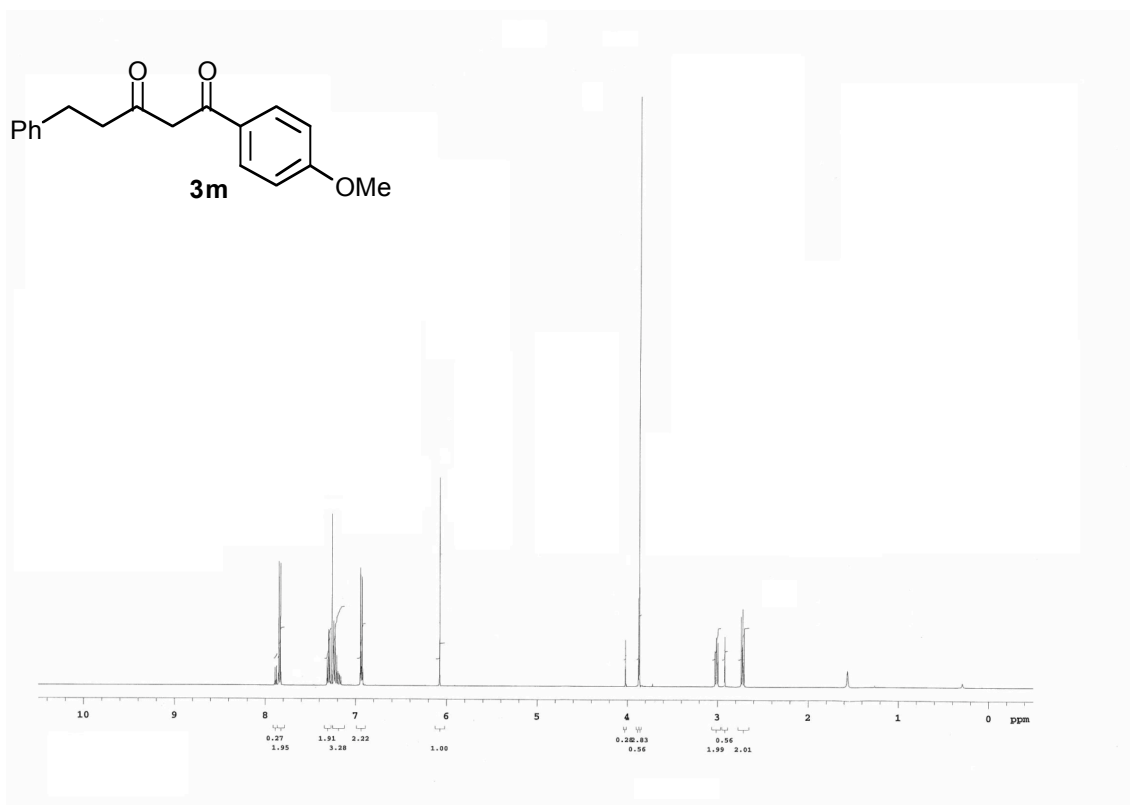


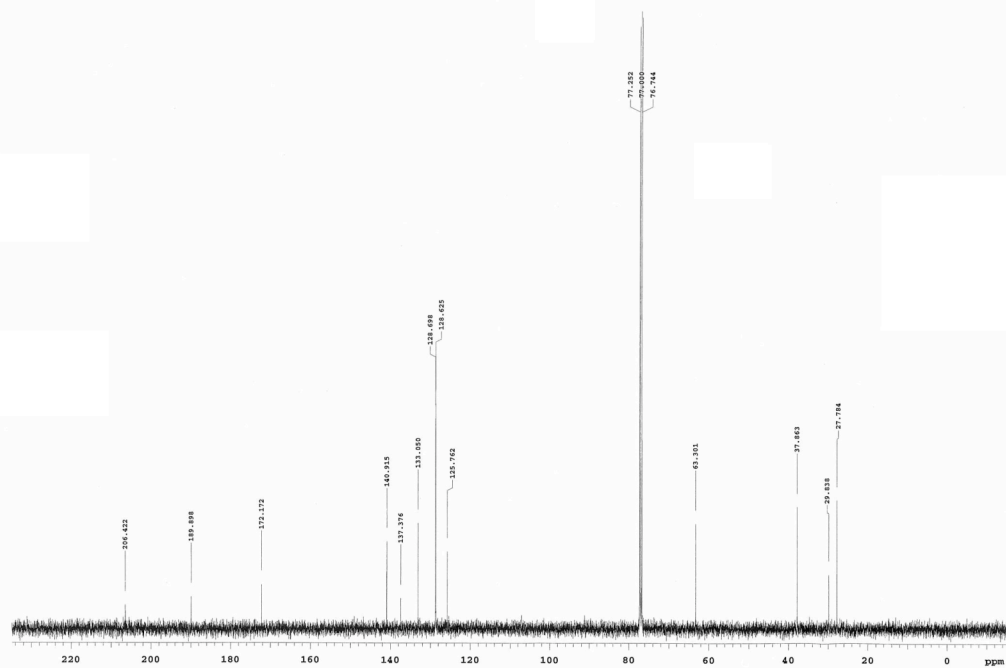
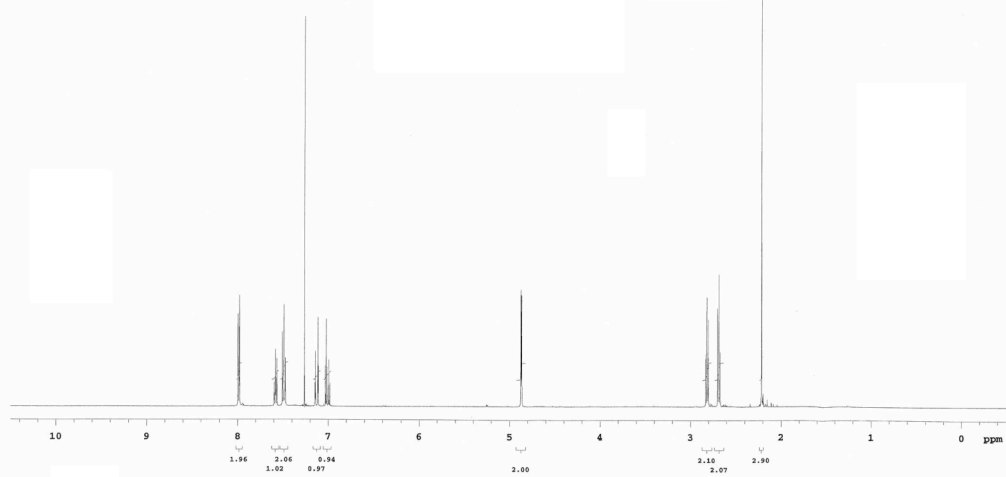
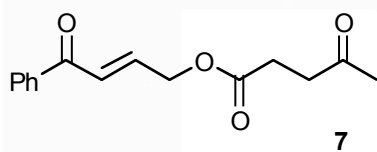


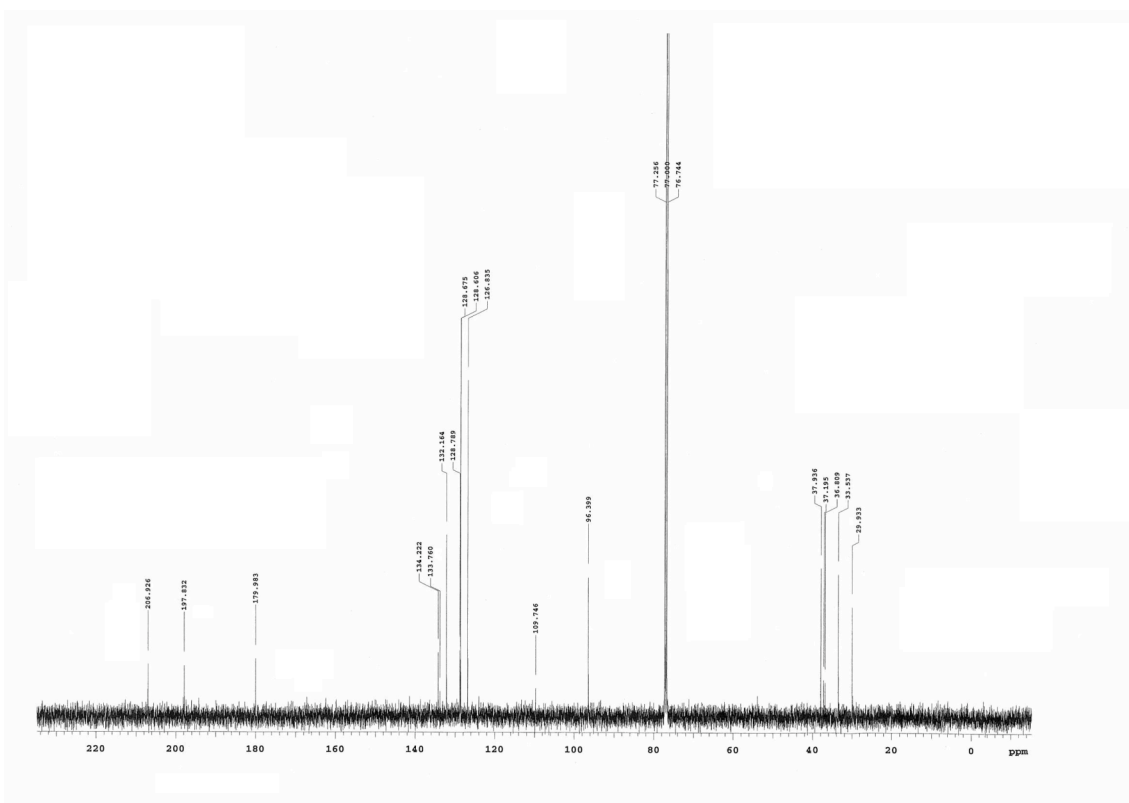
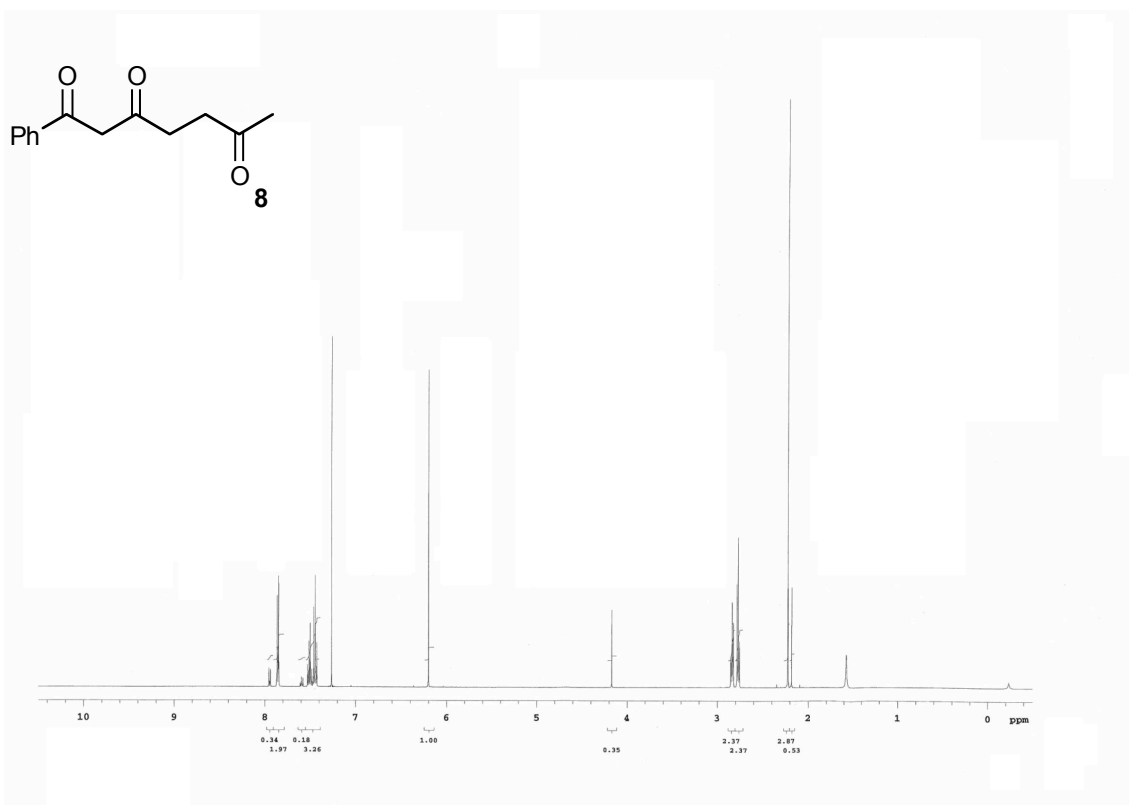


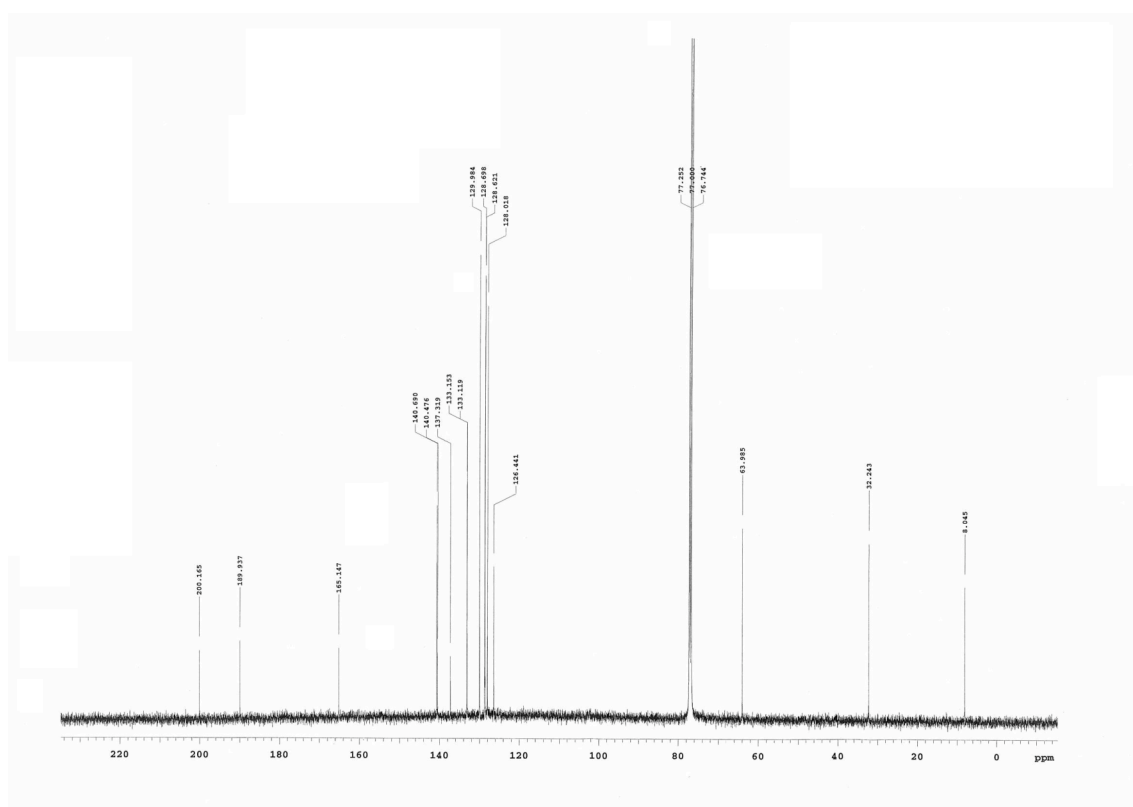
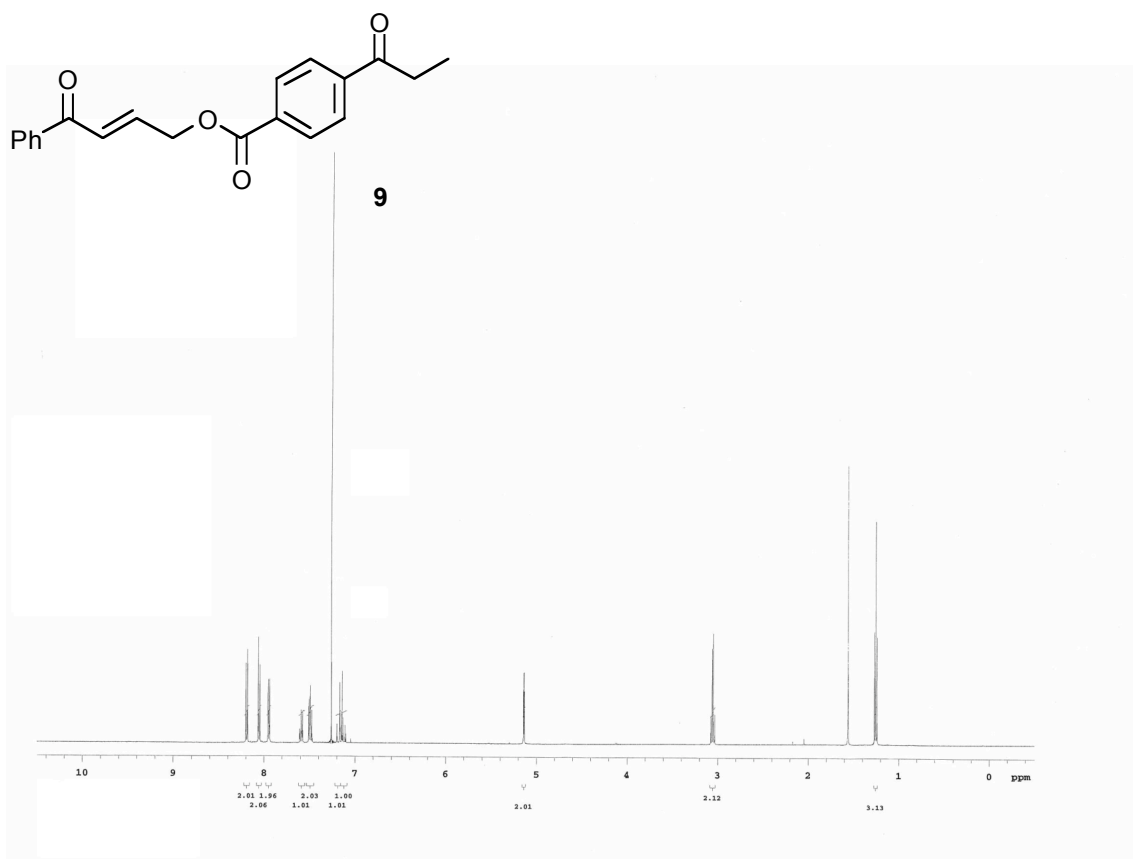


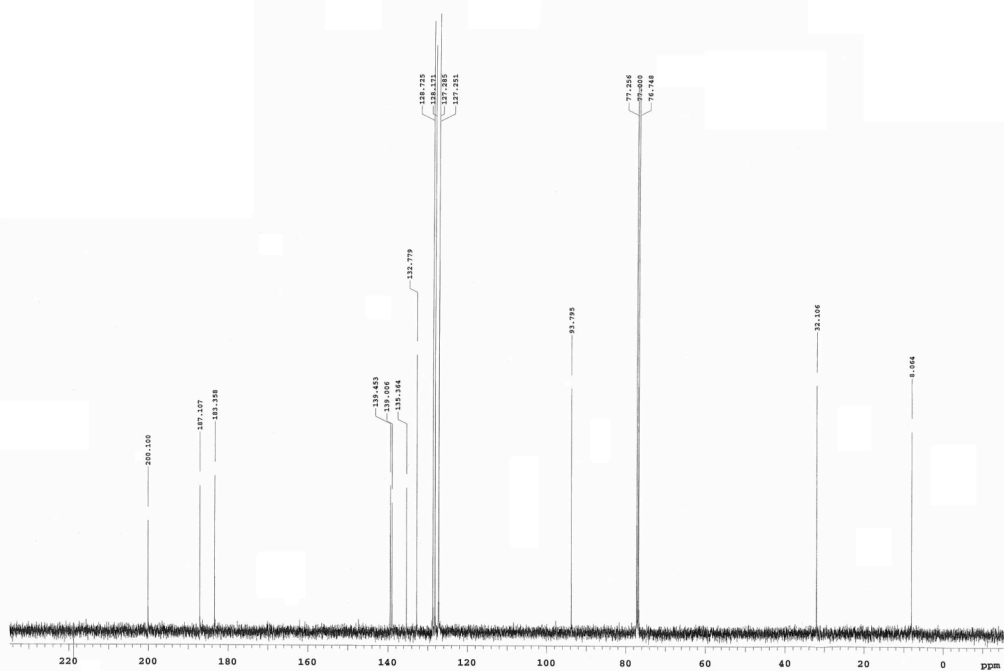
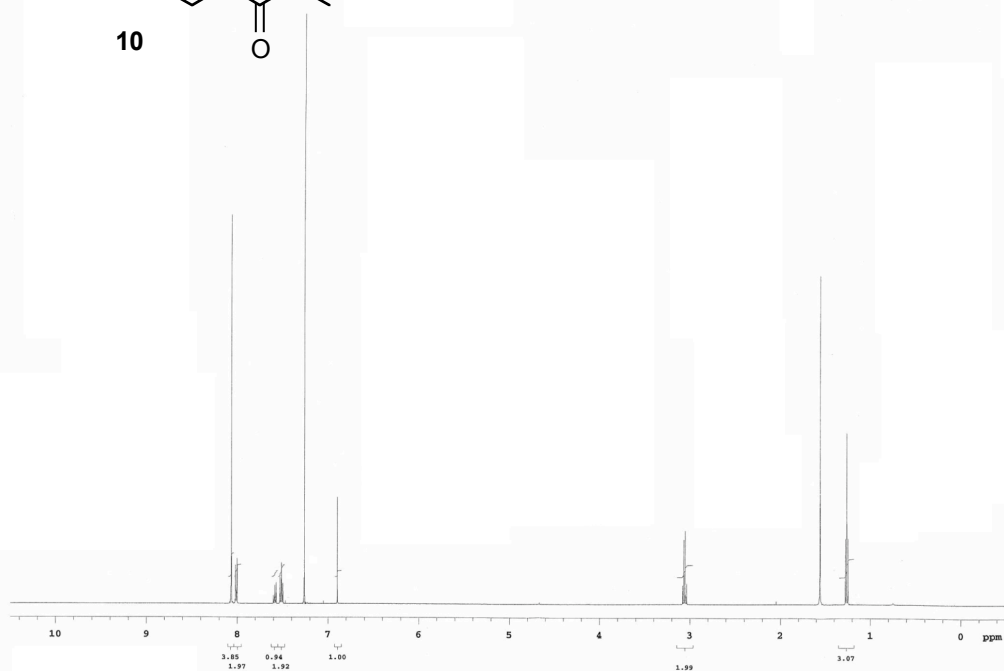
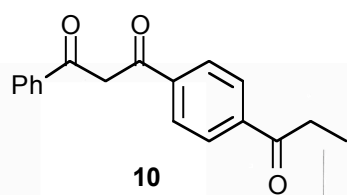


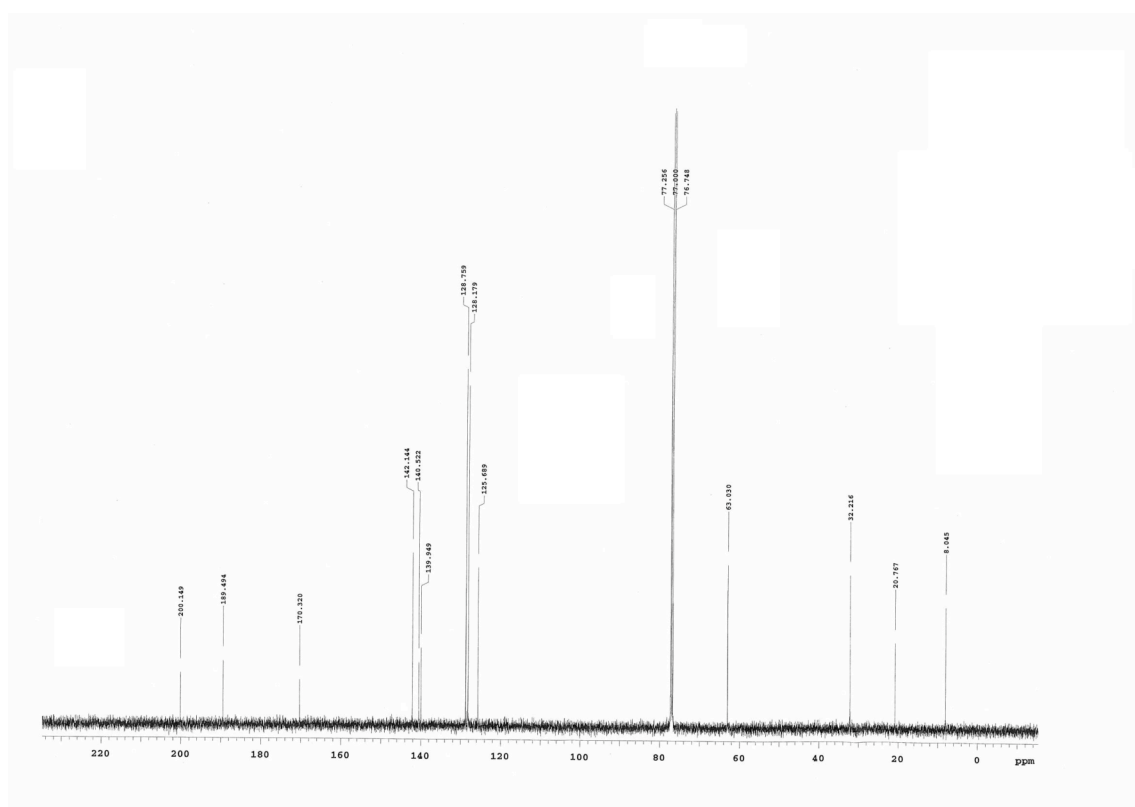
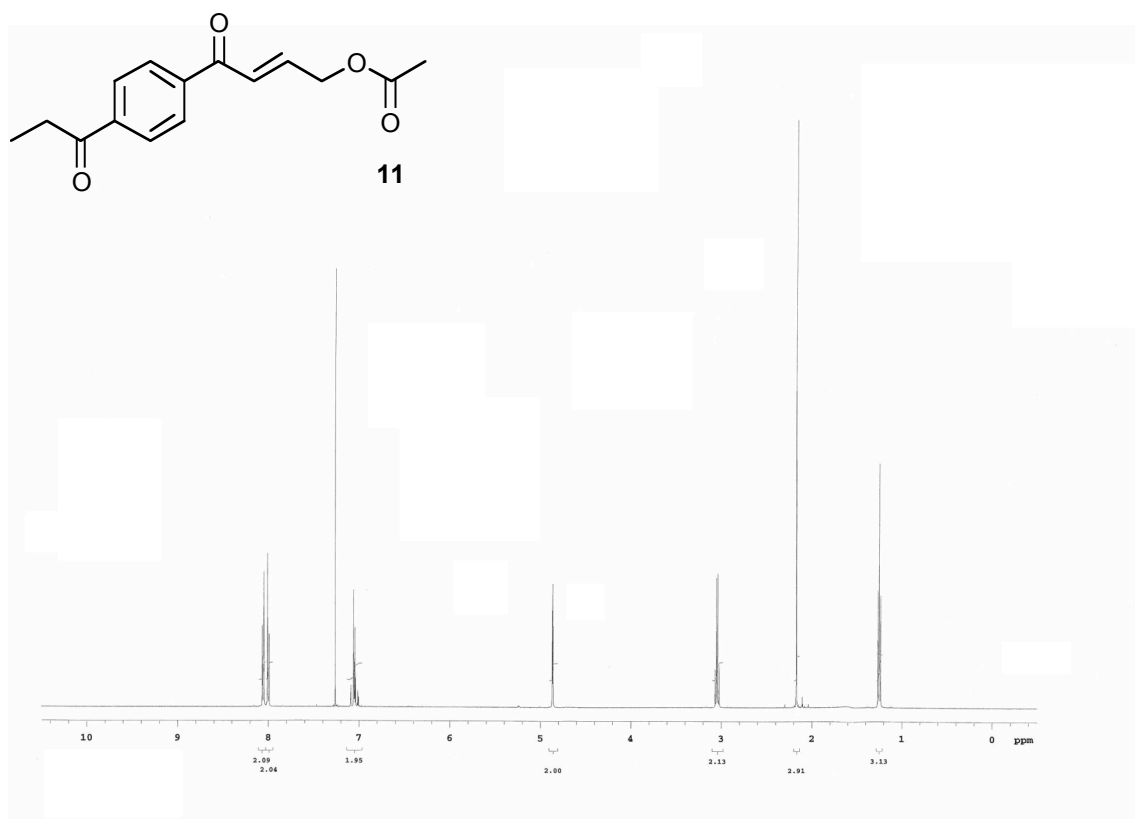


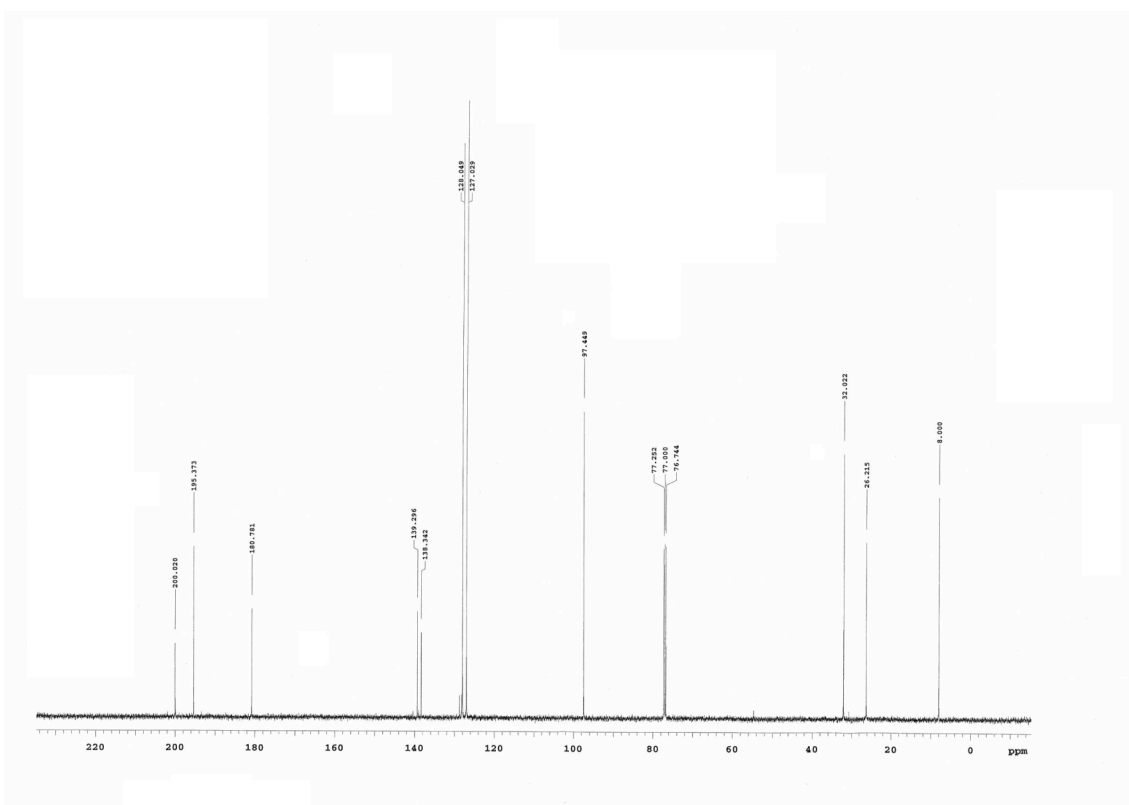
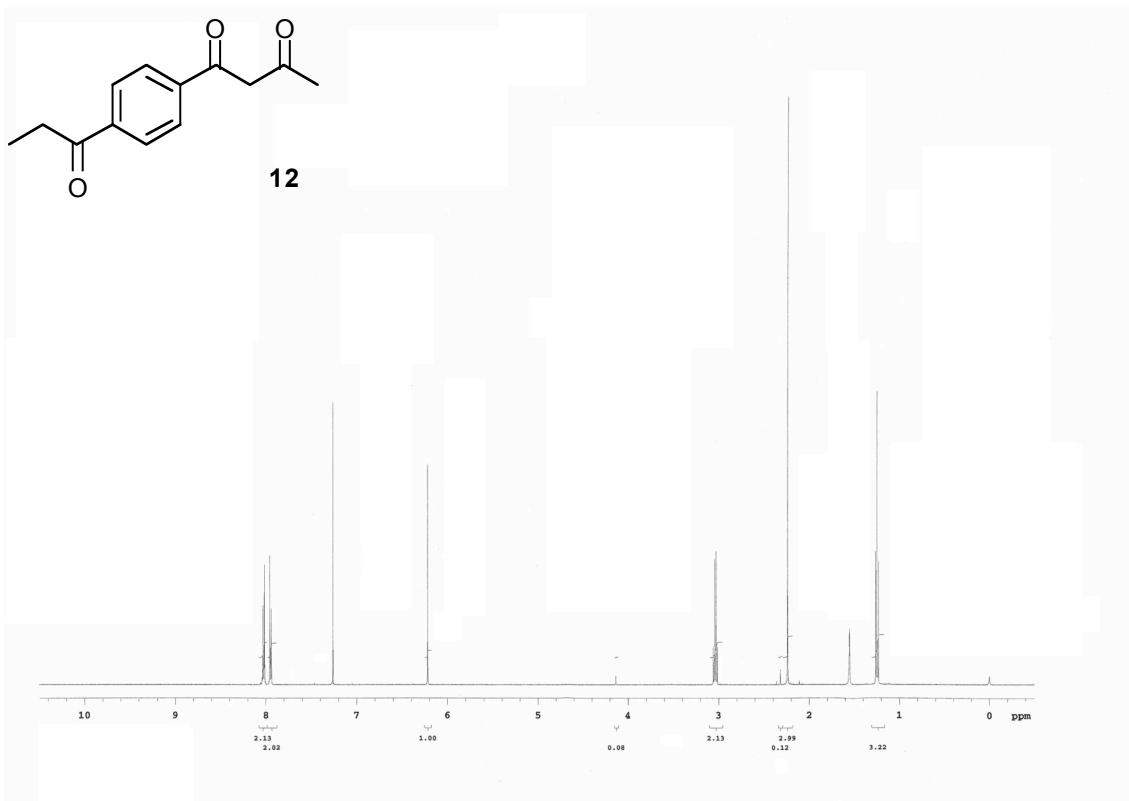


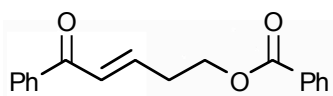




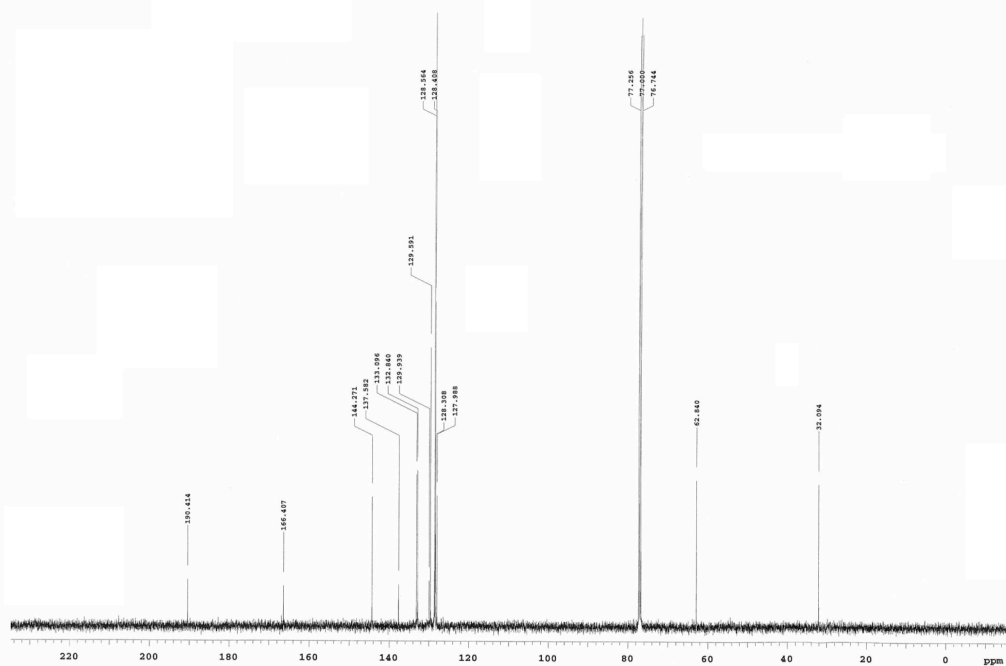
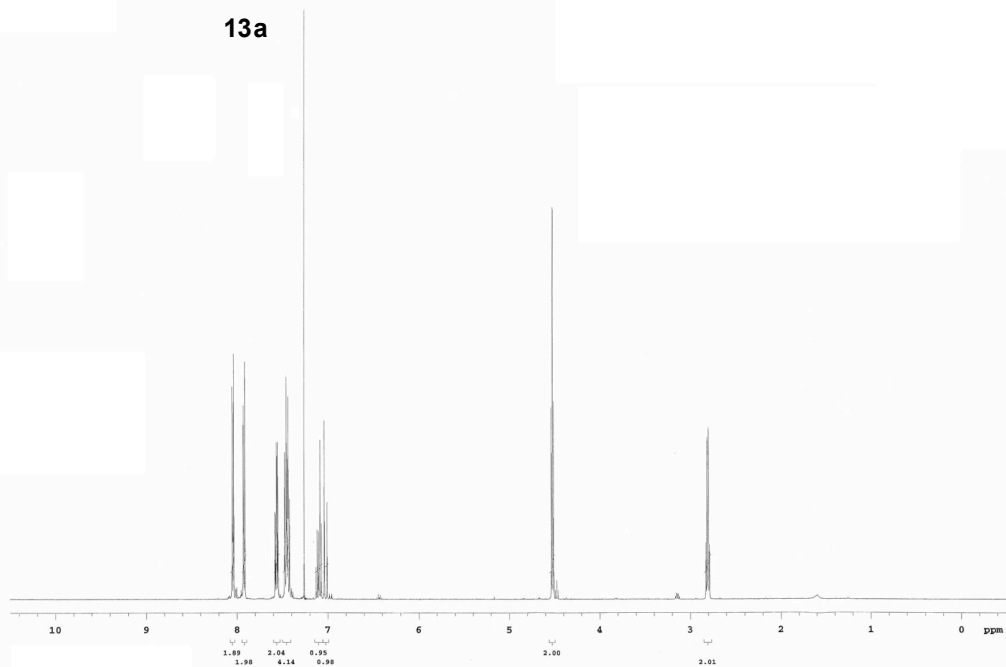


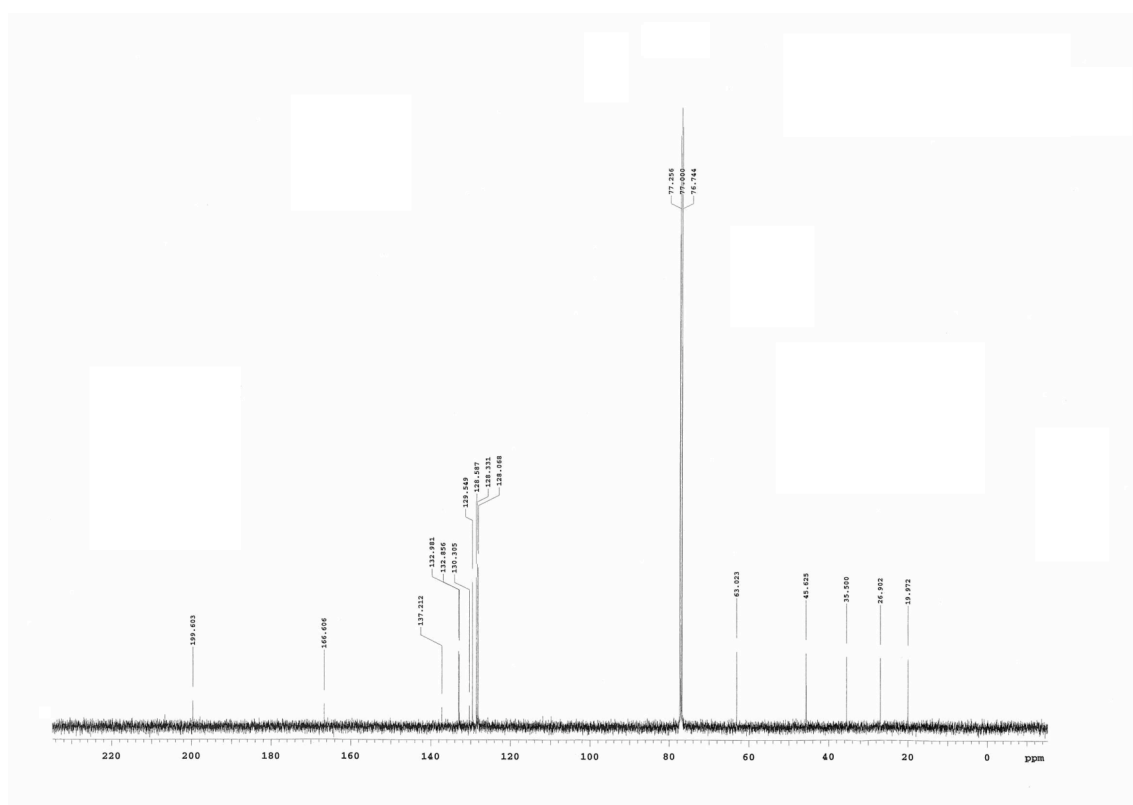
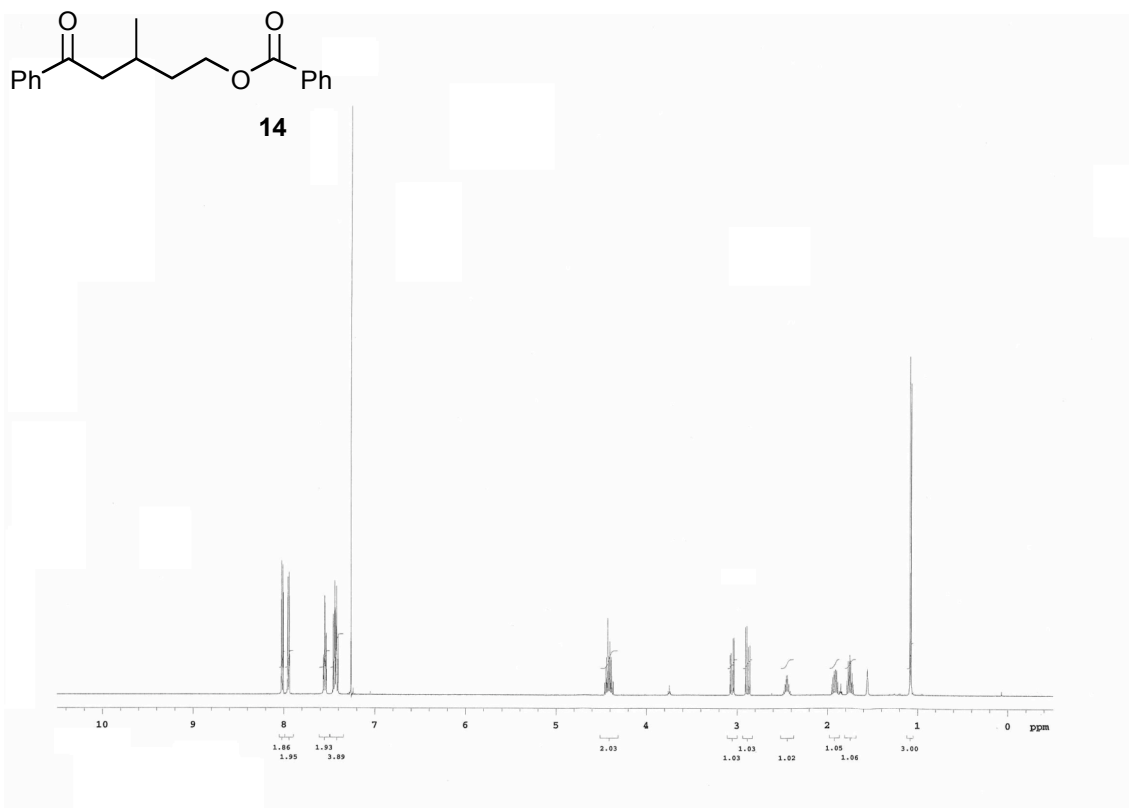


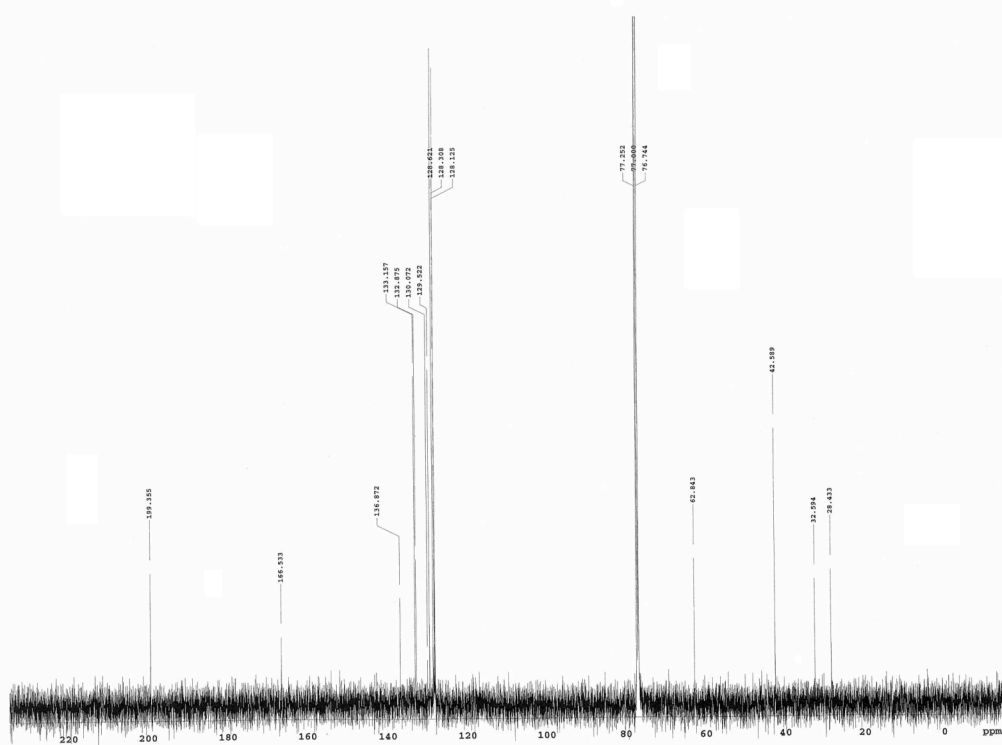
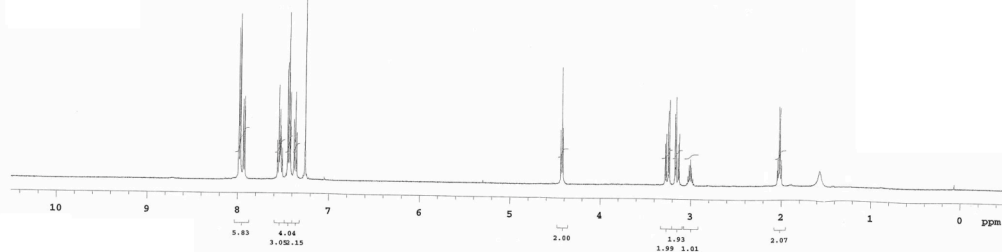
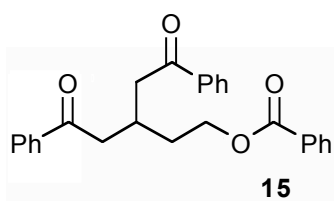


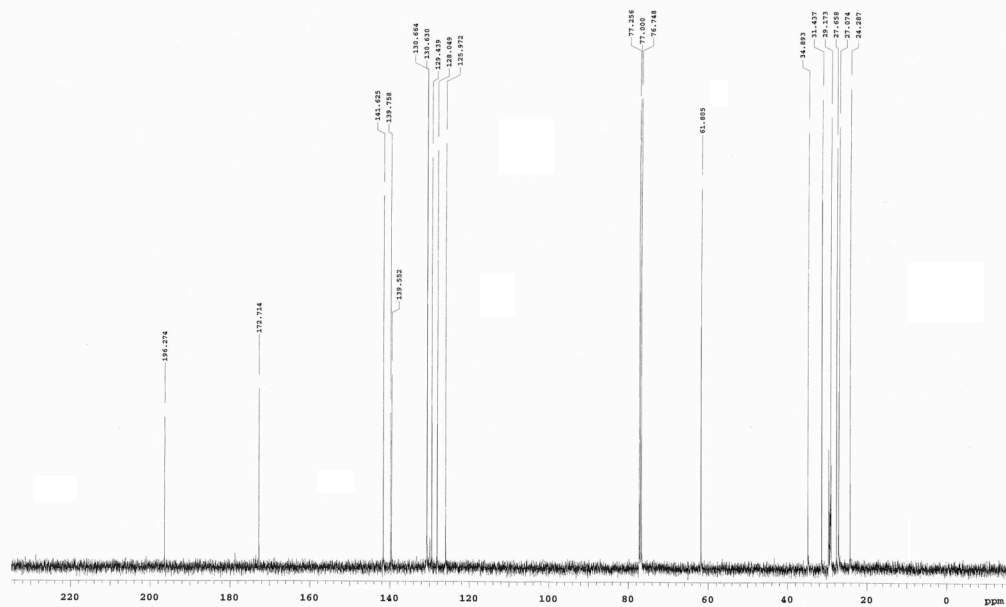
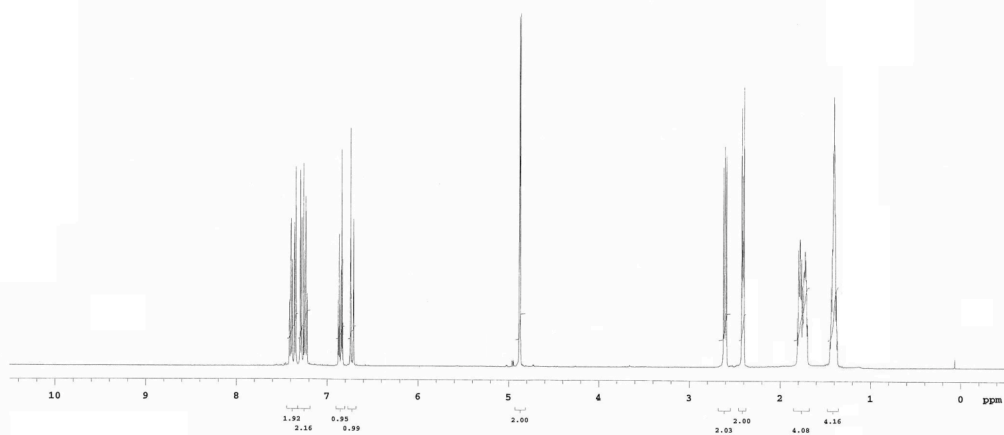
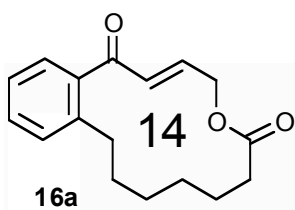


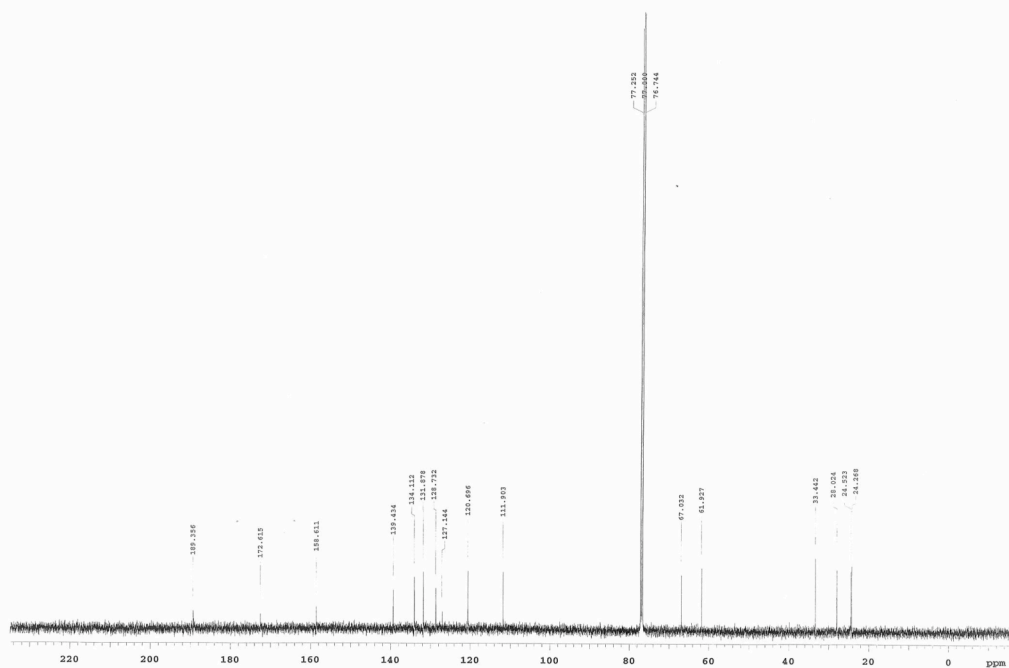
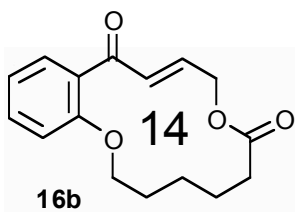
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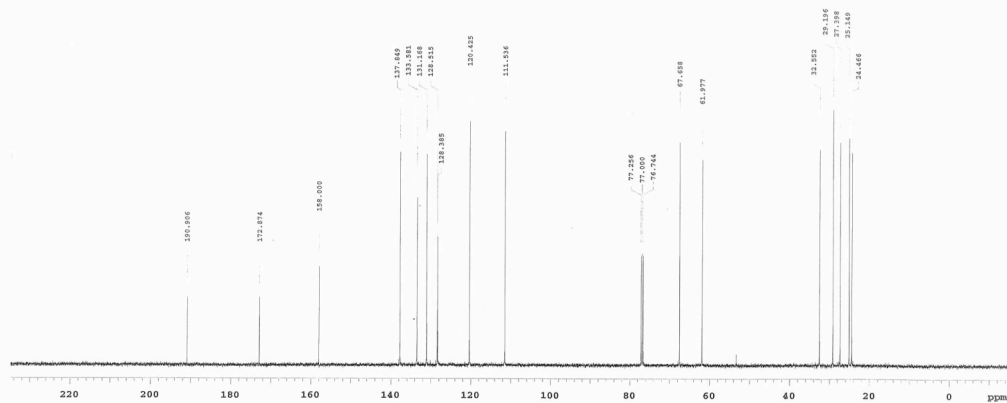
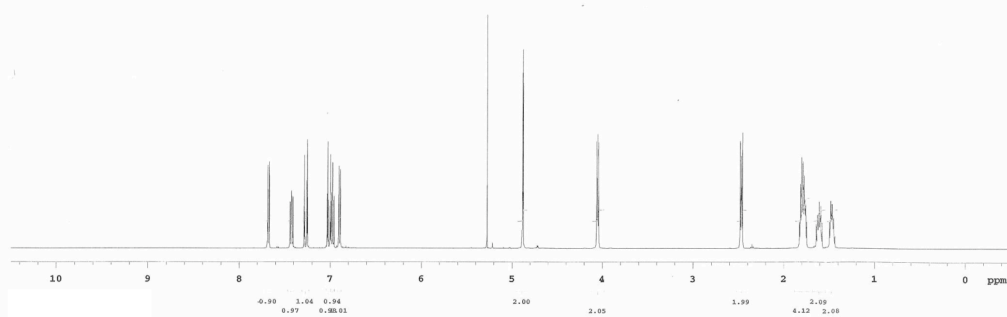
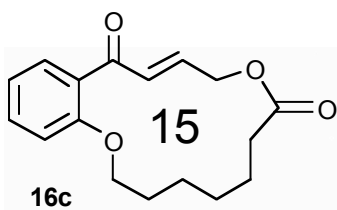


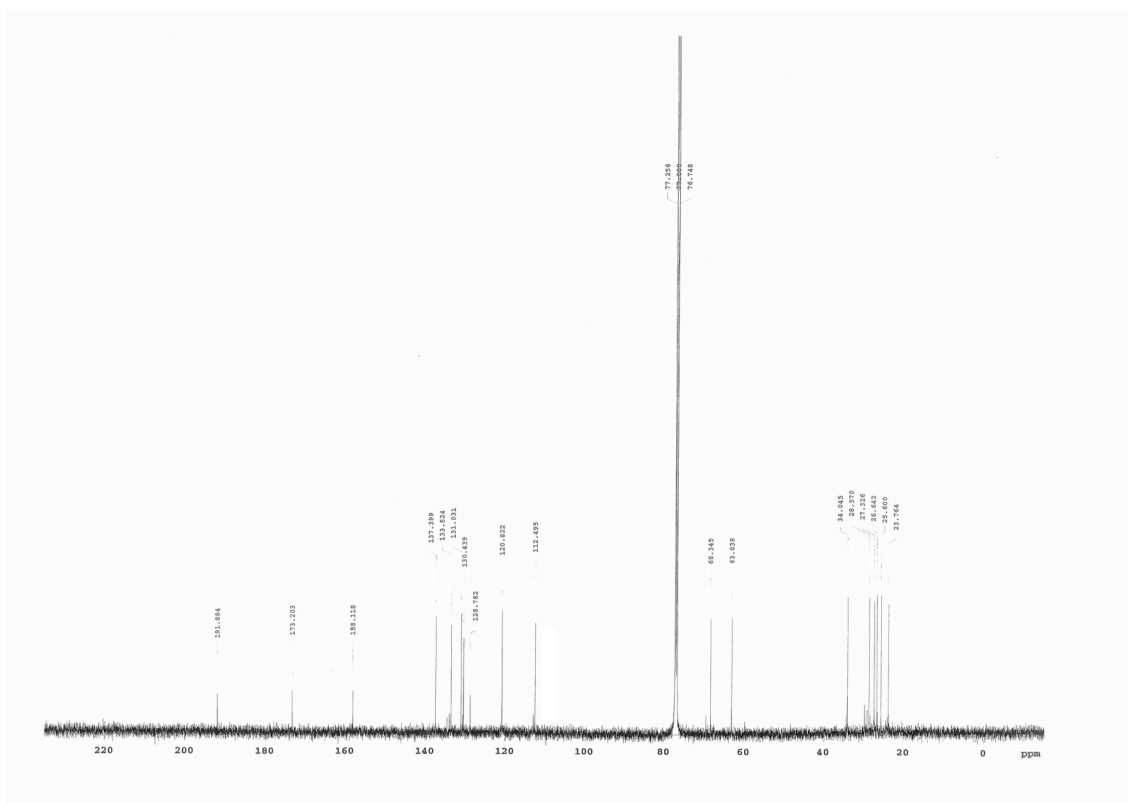
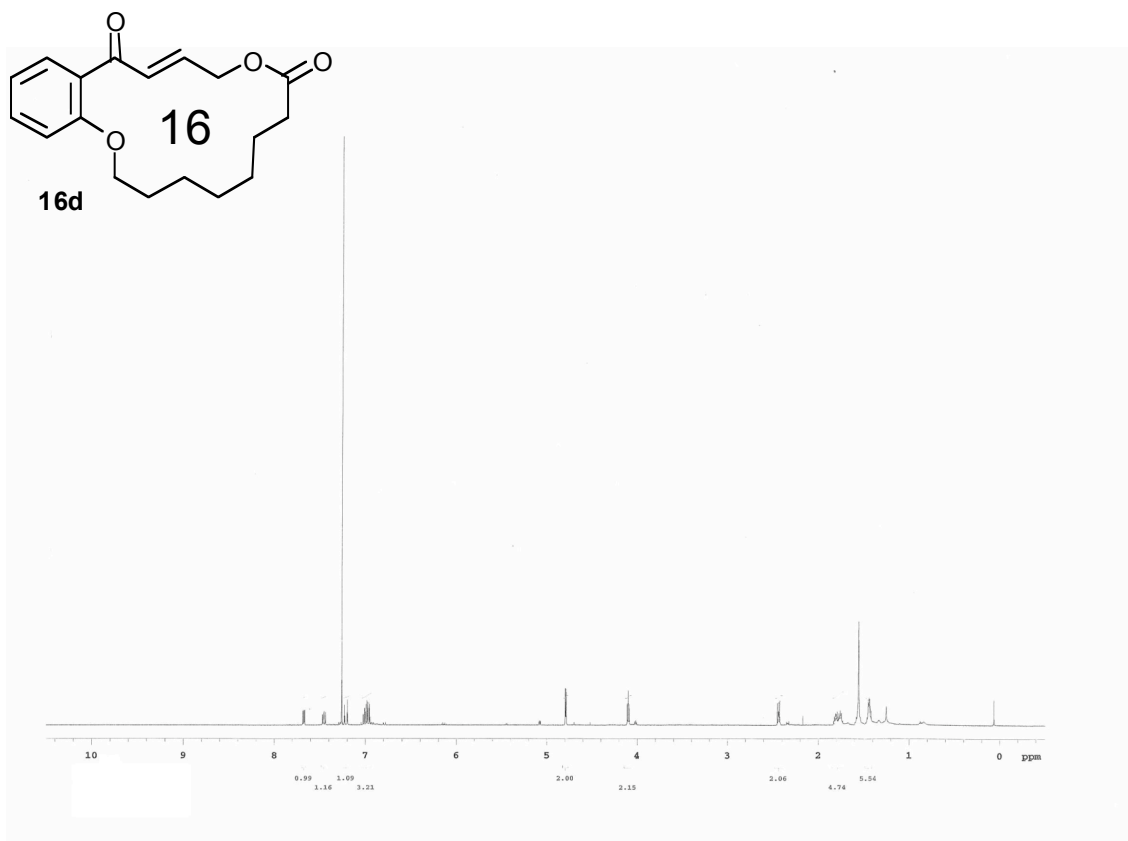


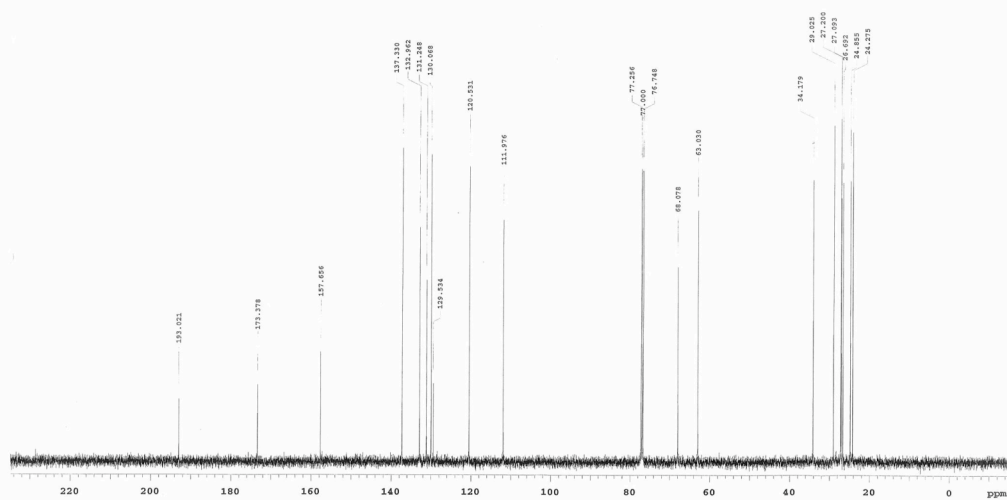
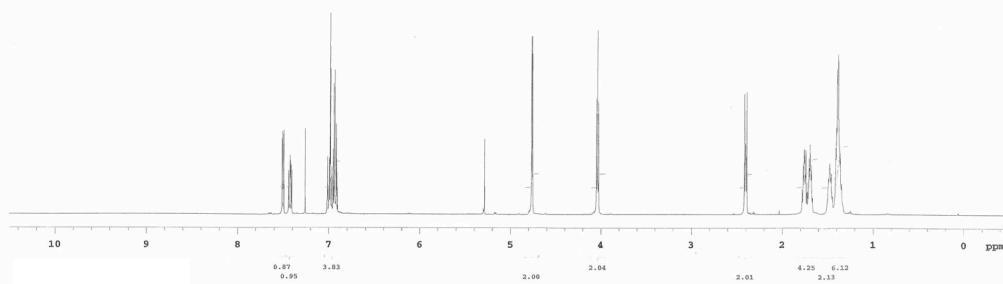
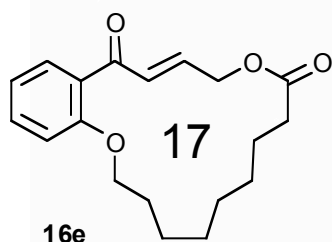


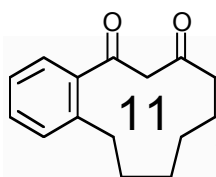












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