

Supporting Information For

Continuous flow synthesis of toxic ethyl diazoacetate for utilization in an integrated microfluidic system

Ram Awatar Maurya,^{a‡} Kyoung-Ik Min,^{b‡} and Dong-Pyo Kim^{*b}

^a Division of Medicinal Chemistry and Pharmacology, CSIR-Indian Institute of Chemical Technology, Hyderabad, India-500007.

^b National Creative Research Center of Applied Microfluidic Chemistry (CAMC), Department of Chemical Engineering, Pohang University of Science and Technology (POSTECH), Pohang, Republic of Korea.. Fax: +82-54-279-5598; Tel:+82-54-279-2272; E-mail: dpkim@postech.ac.kr

General

PFA tubing (id = 500 μm and 800 μm), T-junction, and X-junction were purchased from *Upchurch Scientific*. Common solvents were purchased from Daejung Chemicals. Unless otherwise specified all reagents and chemicals were purchased from Sigma Aldrich and/or Alfa Aesar, and were used without further purification. GC/MS spectrum was recorded by Agilent 5975C GC/MSD System (Agilent Tech., USA/Germany). ^1H NMR and ^{13}C NMR spectra were recorded on a JNM-AL 400. The compounds were characterized by comparing their ^1H and ^{13}C NMR data with literature. All liquid samples were pressure-driven into the channel using syringe pumps (PHD 2000, Harvard Apparatus, USA) in the range of flow rates.

Fabrication of polyimide (PI) film dual channel microseparator

Laser ablation on polyimide film was employed to fabricate the proposed dual channel device as illustrated in Figure S1. First of all, layers of 125 μm thick polyimide films (Kapton HN film, Dupont, USA) were ablated by UV laser (355 nm, ESI, USA) to form linear microchannel (1000 μm width, 80 μm depth and 35 mm length) as previously reported.^[1] The 4-corners of each film were holed (1 mm diameter) to align the film patterns. After laser ablation, the films were cleaned by washing with acetone under ultrasonic and dried. Polytetrafluoroethylene (PTFE) membrane (Whatman, 0.45 μm pore, 37 mm dia) sandwiched by two sheets of polyimide film microchannels were placed between metal holder which align PI films by inserting metal pins through the holes at the film corners. Finally metal holders were tightly assembled by screw to connect tube. To test separation of immiscible organic/aqueous mixture, water with green ink and toluene were introduced into the separator as shown in Fig. S1-b. Because PTFE membrane wets selectively non-aqueous solvents due to hydrophobic nature, water flow only into top channel while toluene phase are wetting on PTFE membrane and are shoved to bottom channel by flowing of water phase. Finally toluene phase were separated from inlet of top channel to outlet of bottom channel. (See supporting movie)

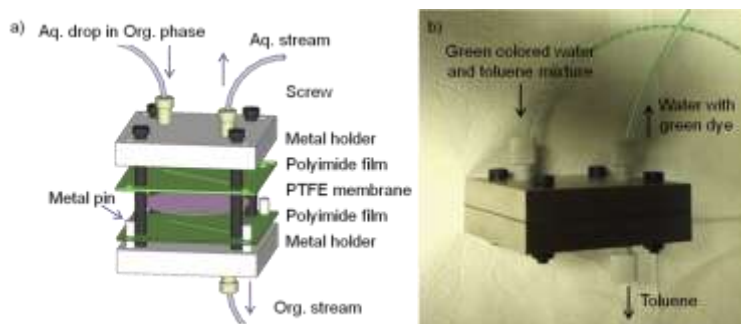


Figure S1. a) Illustration and b) photograph of polyimide film dual channel microseparator.

Preparation of the stock solution of glycine ethyl ester hydrochloride (A):

In a 100 ml volumetric flask, glycine ethyl ester hydrochloride (20.94 g, 150 mmol) and sodium acetate trihydrate (27.22 g, 200 mmol) were taken. DI water was added to the flask with occasional shaking to dissolve the materials and the flask was nearly filled (80-90%). Next pH of the solution was reached to 3.5 by drop-wise addition of glacial acetic acid. Finally DI water was added up to the mark of 100 ml volumetric flask.

Preparation of the stock solution of sodium nitrite (B):

In a 100 ml volumetric flask, sodium nitrite (10.42 g, 151 mmol) was taken and DI water was added with occasional shaking. Finally DI water was added up to the mark of 100 ml volumetric flask.

Typical experimental procedure for in-situ synthesis, extraction, and separation of EDA:

20 ml of the stock solution A and 20 ml of the stock solution B were taken separately using two glass syringes, and were mounted on a syringe pump (PHD 2000, Harvard Apparatus, dual syringe pump). Third glass syringe taken 20 ml of toluene was mounted on another similar syringe pump. Next the capillary microreactor and PI dual channel separator (as shown in Figure S2a and S2b) were connected to the syringes (A, B and the one having toluene) using disposable needle (or an Upchurch connector). Both the syringe pumps were set at the same flow rate and were switched on at room temperature. The detailed specification is below;

PFA capillary reactor: ID = 800 μm , length = 120 cm, internal volume = 600 μL .

Flow rate ratio of aq. solutions (A and B) and extracting solution was 1:1:1.

Residence time for both droplet reaction and extraction was (50+50+50) $\mu\text{L}/\text{min}$ for 4 min, (75+75+75) $\mu\text{L}/\text{min}$ for 2.7 min, (100+100+100) $\mu\text{L}/\text{min}$ for 2 min, (150+150+150) $\mu\text{L}/\text{min}$ for 1.3 min of the residence time.

EDA samples were collected from the outlet of PI dual channel separator. The first few ml of the samples (4-5 ml) were discarded (10-30 min for each flow rate) and then the samples were collected for a specified interval of time.

Calculation of EDA yield:

EDA from Aldrich was degassed in vacuum to remove residual dichloromethane impurities. After confirming complete removal of dichloromethane by GC-MS, several standard solutions of the EDA (1.5 M, 1.0 M, 0.75 M, and 0.50 M) in toluene containing different amounts of anisole (0.15 M, 0.10 M, 0.075 M, and 0.005 M) were prepared. Standard samples were run on a GC-MS instrument to obtain standard graphs and the ratio of areas below the EDA and anisole signal were calculated. Next calculated amount of anisole was added to the synthesized EDA samples from outlet of PI dual channel separator and the resulting samples were run on GC-MS to obtain the sample graph. The yield of EDA was calculated by comparing the graphs of standard solutions and sample EDA solutions.

In-situ synthesis, extraction, and separation of EDA:

In-situ synthesis, extraction, and separation of EDA were carried out by introducing glycine ethyl ester hydrochloride in acetate buffer (pH = 3.5), aqueous NaNO₂, and extracting solvent to the microfluidic set-up. Initially we attempted to mix the aqueous solutions of glycine and NaNO₂ and then dispersed that mixture into toluene using two T-junctions (Figure S2a). However, there was a significant loss of EDA when two T-junctions were used, although cooling of the reaction mixture in ice bath diminished the degradation. We, therefore, decided to use an X-junction (Figure S2b) for mixing the two aqueous solutions for instant dispersion of mixture into extracting solvent to minimize the decomposition of EDA in acidic medium. The results of EDA synthesis using two T-set and one X- junction are comparatively summarized in Table S1.

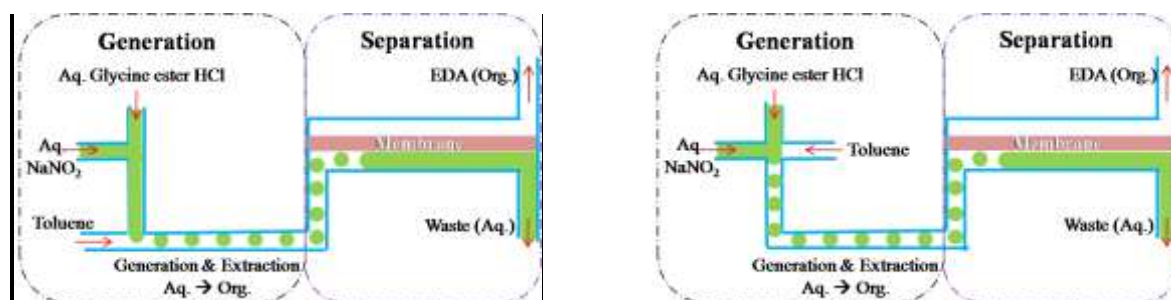


Figure S2a (left) & S2b (right)

Table S1. Results of EDA synthesis using two T-set (Figure S2a) and one X-junction (Figure S2b)

$\text{H}_2\text{N}-\text{CH}_2-\text{C}(=\text{O})-\text{O}-\text{CH}_2\text{CH}_3 \cdot \text{HCl} \xrightarrow{\text{NaOAc, NaNO}_2/\text{HCl}} \text{N}_2=\text{CH}-\text{C}(=\text{O})-\text{O}-\text{CH}_2\text{CH}_3$					
Entry ^a	Temp. (°C)	Mixing device	Extracting solvent	Res. Time ^[b]	Yield (%) ^[c]
1	rt	2 T-set	Toluene	2.0 min	60
2	0	2 T-set	Toluene	2.0 min	91
3	rt	X- junction	Toluene	2.0 min	99

[a] Composition of EDA precursors: 1.50M EtOOCCH₂NH₂.HCl in acetate buffer (pH=3.5), 1.51M NaNO₂ in water; flow rates of aq. solutions and extracting solution were in 1:1:1 ratio. [b] Residence time for droplet reaction and extraction in PFA capillary (id = 800 μm, length = 120 cm). [c] Determined by GC/MS using anisole as an internal standard.

General experimental procedure (cascade aldol reaction with aldehydes):

20 ml of stock solution A, 20 ml of stock solution B, and 20 ml of extracting solvent (toluene) were taken in three separate glass syringes, and introduced to X-junction at identical flow rates. The X-junction was connected to PI dual channel microseparator via PFA tube (id = 800 μm , length = 120 cm, internal volume = 600 μL). The out-coming organic phase containing EDA (1.5 M) from PI dual channel separator was allowed to mix with the toluene solutions of DBU (1.2 M) and aldehydes (6.0 M) respectively through X-junctions (Figure S3). The final reaction mixture (EDA, DBU, and aldehyde) was then passed through ultrasonication (power = 330 W, frequency = 40 KHz, 40 $^{\circ}\text{C}$) using a PFA capillary (id = 800 μm , length = 5 m, internal volume = 2.5 mL) and the reaction was quenched into aqueous NaHCO_3 . In detail, after setting the flow rates of the various syringes on the digital syringe pump, first the syringe pumps having stock solution A, B, and extracting toluene were stitched on. When toluene solution containing EDA started coming out from the outlet of PI dual channel separator and approached to the next T or X junction, the rest of the syringe pumps (aldehyde and DBU) were switched on (flow rates of EDA and benzaldehyde containing DBU: (50+20) $\mu\text{L}/\text{min}$ for 36 min, (75+30) $\mu\text{L}/\text{min}$ for 24 min, (100+40) $\mu\text{L}/\text{min}$ for 18 min of the residence time). After turning on the aldehyde/DBU syringe pumps, sometimes incomplete separation of aqueous-organic phases in the PI dual channel separator was happened due to increased back pressure in the organic layer. In such cases, the increased tubing length of the aqueous outlet of PI dual channel separator ensured complete aqueous-organic separation by counterbalancing the back pressures. Upon stable flow with complete aqueous-organic separation, the first few ml of the samples (4-5 ml) were discarded and then exactly 5 mmol of the product was collected (Run time 55.6 min). The temperature of ultrasonication bath was maintained constant by continuous water circulation (40, 60 and 80 $^{\circ}\text{C}$, respectively). The organic phase was separated, dried, and evaporated to yield the product mixture which was purified by silica-gel column chromatography.

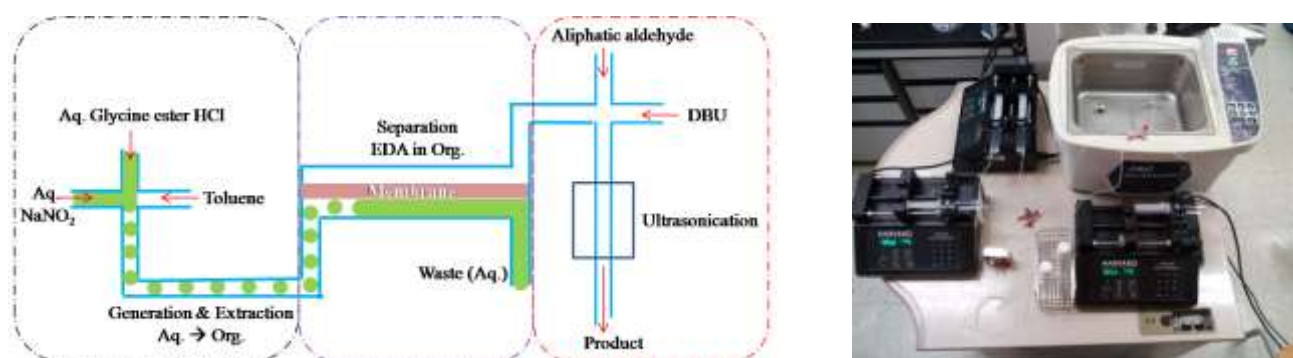


Figure S3. Microreactor set-up for cascade generation, separation, and reaction of EDA with aldehyde

General experimental procedure (cascade 2-keto ester synthesis):

20 ml of stock solution A, 20 ml of stock solution B, and 20 ml of extracting solvent (toluene) were taken in three separate glass syringes and introduced to X-junction at identical flow rates. The X-junction was connected to PI dual channel microseparator via PFA tube (id = 800 μm , length = 120 cm, internal volume = 600 μL). The out-coming organic phase (EDA) from PI dual channel separator was allowed to mix with toluene solution of aldehydes (3.0 M) containing 5 mol% of $\text{BF}_3\cdot\text{OEt}_2$ through T-junction. The final reaction mixture was then passed through a PFA capillary (id = 800 μm , length = 5.0 m, internal volume = 2.5 mL) which was connected with another PI dual channel gas-liquid separator device. Finally the reaction was quenched into aqueous NaHCO_3 . In detail, when toluene solution containing EDA coming out from the outlet of PI dual channel separator approached to the next T junction, the syringe pump taking the aldehyde solution containing $\text{BF}_3\cdot\text{OEt}_2$ was switched on. The same procedure as the above aldol reaction was applied in the other cases. Finally 5 mmol of the product was collected. The organic phase was separated, dried, and evaporated to yield the product mixture which was purified by silica-gel column chromatography.

Calculation of EDA production/Day (As per Table 1):

The concentration of EDA in extracted toluene phase = $1.50 \text{ mole/L} \times 0.99 = 1.485 \text{ mole/L}$

Total volume of EDA solution (in toluene) produced in a day = $100 \text{ uL/min} \times 1440 \text{ min} = 144 \text{ mL}$

Amount of EDA produced per day = $1.485 \text{ mole/L} \times 144 \text{ mL} = 213.84 \text{ mmole}$

Calculation of the production of benzaldehyde-EDA adduct 2a/Day (As per Table 2):

The optimized yield for **2a** = 81%

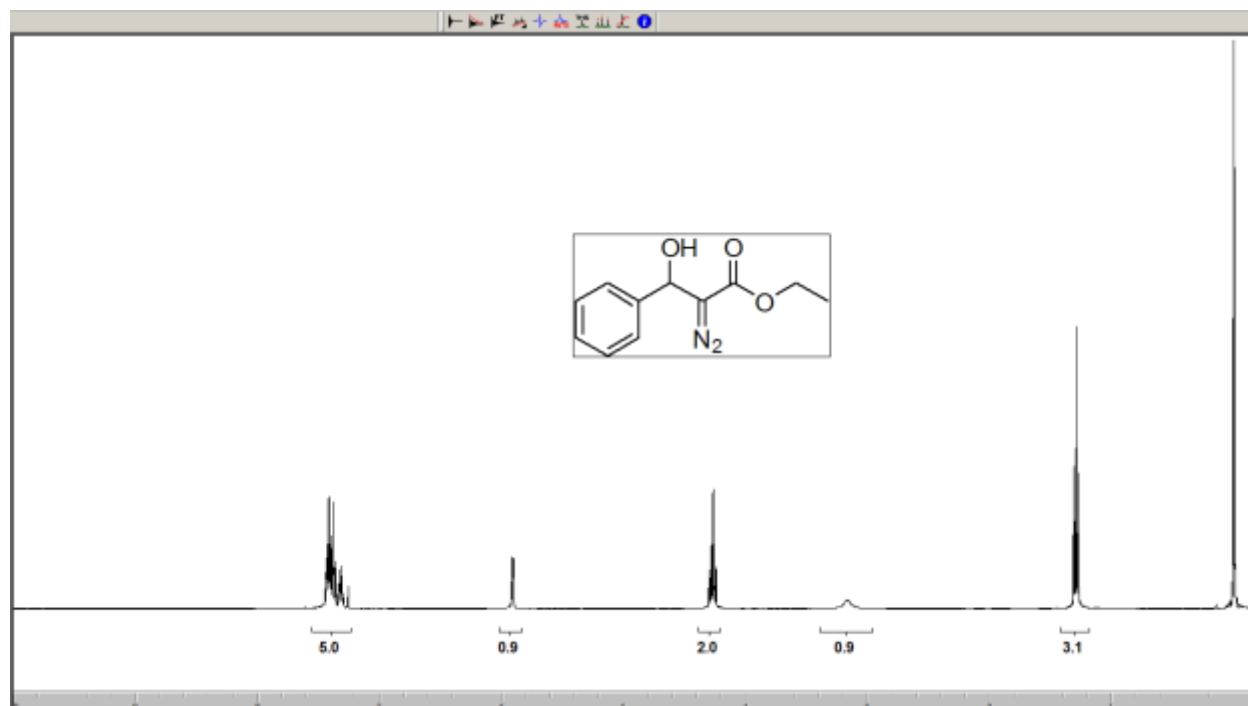
Total mM of benzaldehyde reacted in a day = $30 \text{ uL/min} \times 1440 \text{ min} \times 3 \text{ mole/L} = 129.6 \text{ mmole}$

Amount of **2a** produced per day = $129.6 \text{ mmole} \times 0.81 = 104.98 \text{ mmole}$

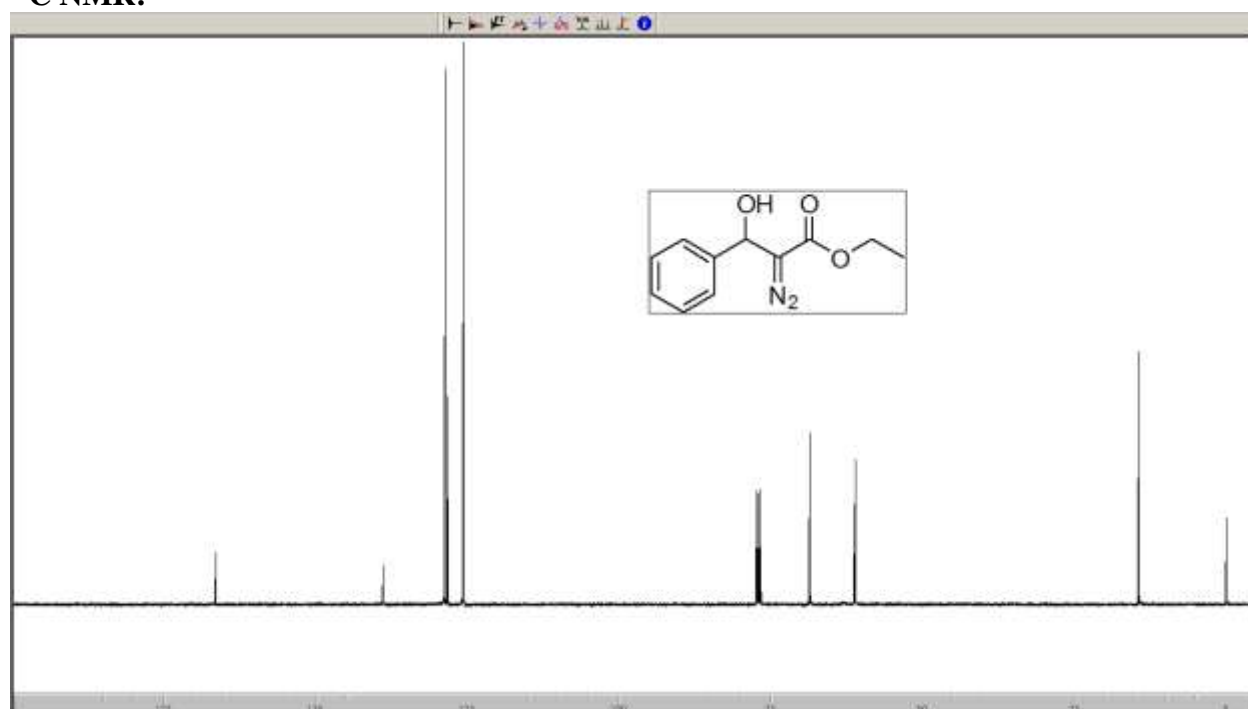
Characterization data for synthesized compounds:

Ethyl 2-diazo-3-hydroxy-3-phenylpropanoate (2a):^[2] Mass (EI): $m/z = 220$ (M^+); ^1H NMR (CDCl_3 , 400MHz) δ : 1.28 (t, $J = 7.07$, 3H), 3.16 (bs, 1H), 4.25 (q, $J = 7.07$ Hz, 2H), 5.91 (s, 1H), 7.26-7.44 (m, 5H); ^{13}C NMR (CDCl_3 , 100MHz) δ : 14.46, 61.20, 68.65, 125.71, 128.27, 128.73, 138.95, 166.46.

^1H NMR:

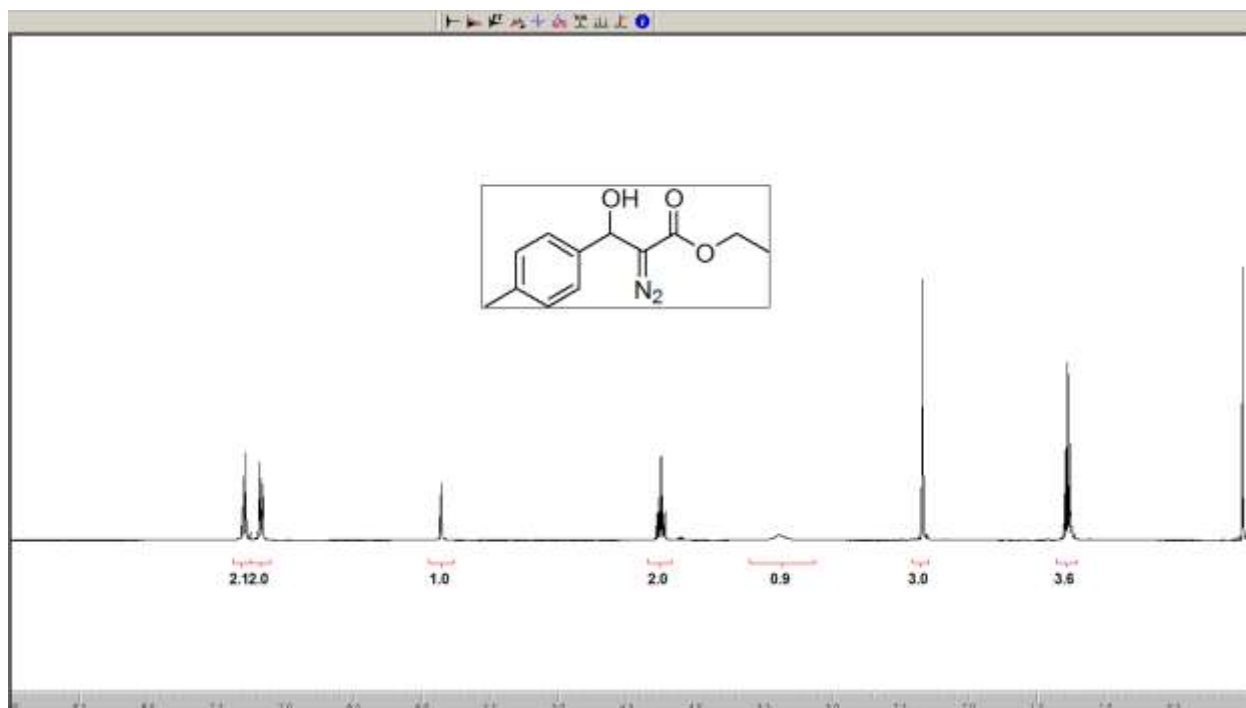


^{13}C NMR:

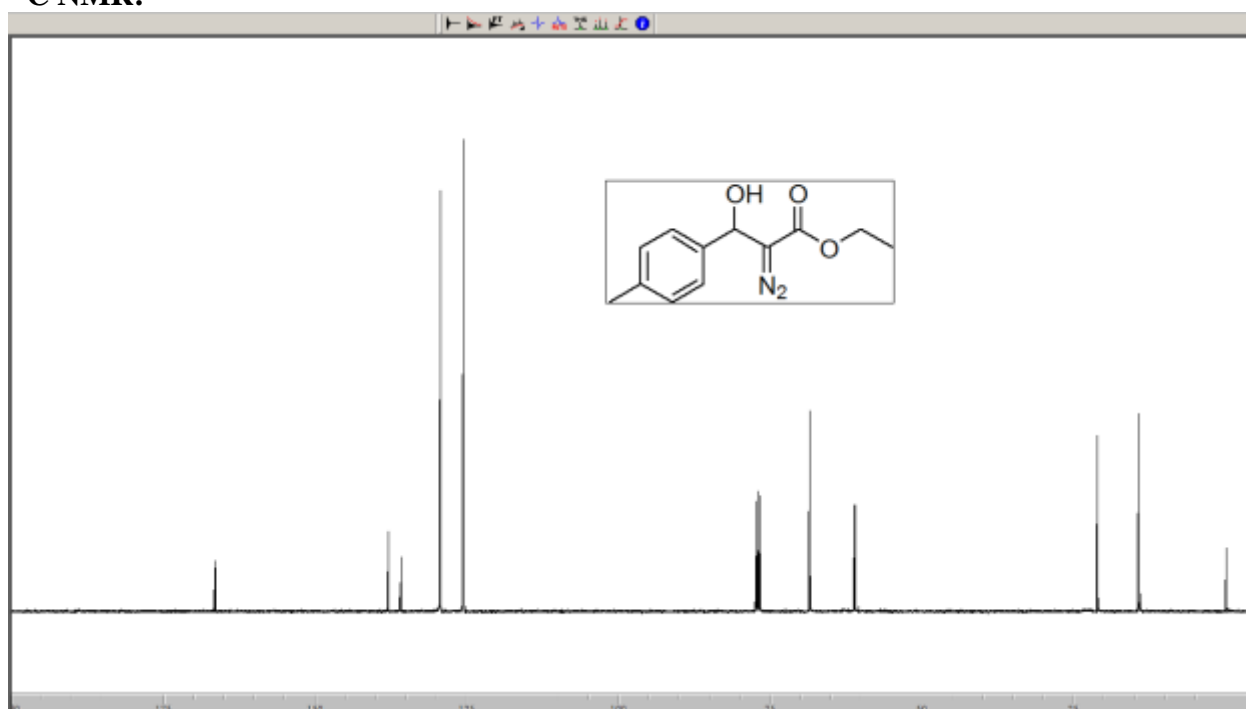


Ethyl 2-diazo-3-hydroxy-3-*p*-tolylpropanoate (2b):^[3] Mass (EI): $m/z = 234$ (M^+); ^1H NMR (CDCl_3 , 400MHz) δ : 1.26 (t, $J = 7.07$, 3H), 2.34 (s, 3H), 3.39 (bs, 1H), 4.23 (q, $J = 7.07$ Hz, 2H), 5.86 (s, 1H), 7.17 (d, $J = 8.04$ Hz, 2H), 7.29 (d, $J = 8.04$ Hz, 2H); ^{13}C NMR (CDCl_3 , 100MHz) δ : 14.46, 21.15, 61.15, 68.55, 125.63, 129.39, 135.95, 137.99, 166.51.

^1H NMR:

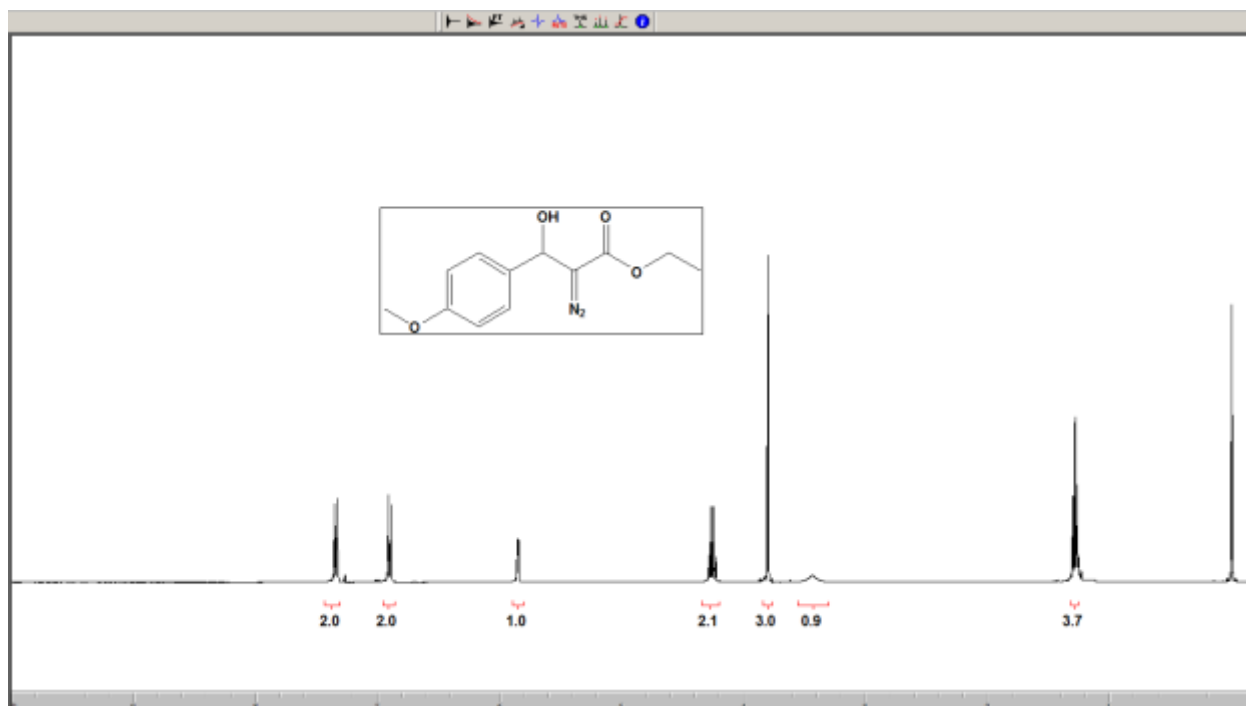


^{13}C NMR:

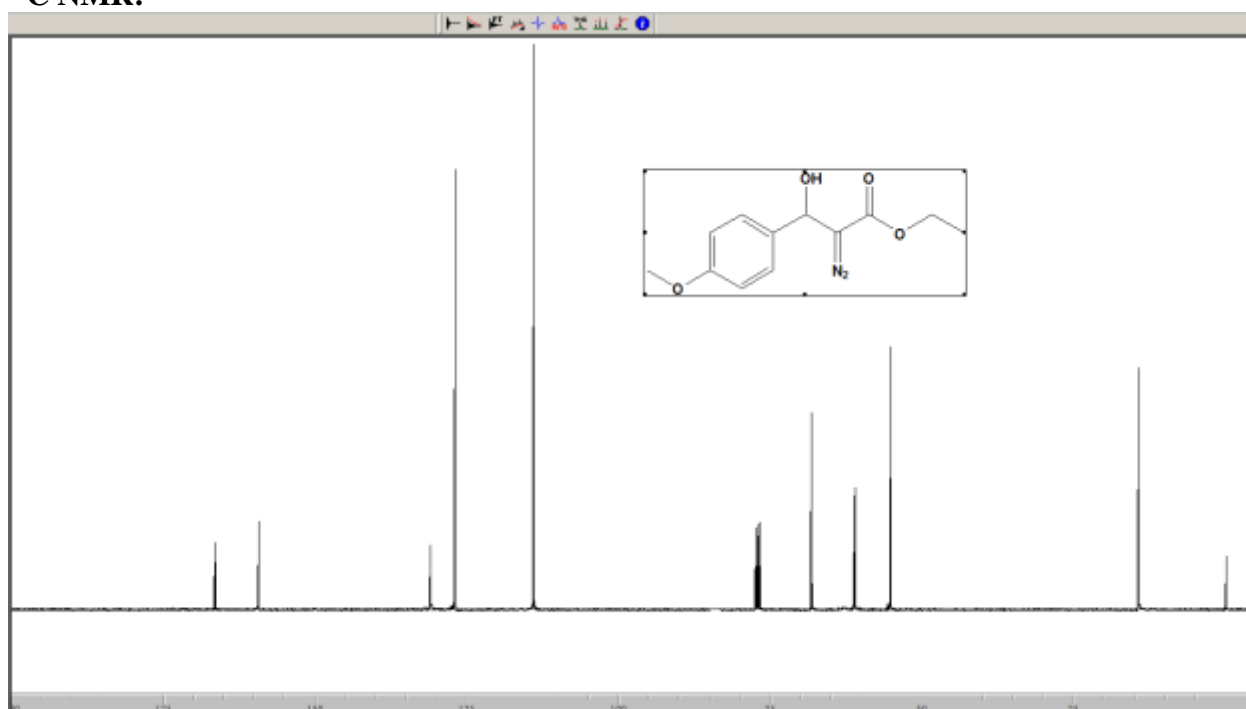


Ethyl 2-diazo-3-hydroxy-3-(4-methoxyphenyl)propanoate (2c):^[2] Mass (EI): $m/z = 250$ (M^+); ^1H NMR (CDCl_3 , 400MHz) δ : 1.27 (t, $J = 7.07$, 3H), 3.44 (bs, 1H), 3.80 (s, 3H), 4.23 (q, $J = 7.07$ Hz, 2H), 5.86 (s, 1H), 6.89 (d, $J = 8.29$ Hz, 2H), 7.33 (d, $J = 8.29$ Hz, 2H); ^{13}C NMR (CDCl_3 , 100MHz) δ : 14.45, 55.26, 61.15, 68.25, 114.06, 126.99, 131.11, 159.41, 166.51.

^1H NMR:

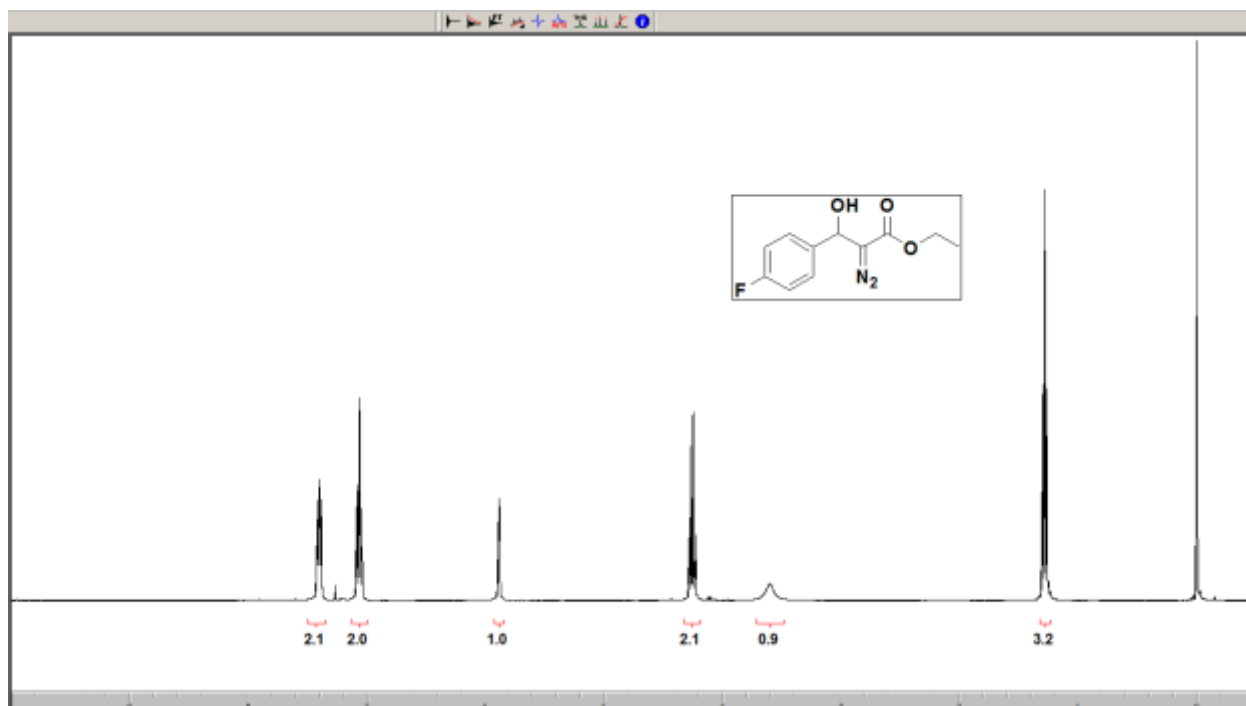


^{13}C NMR:

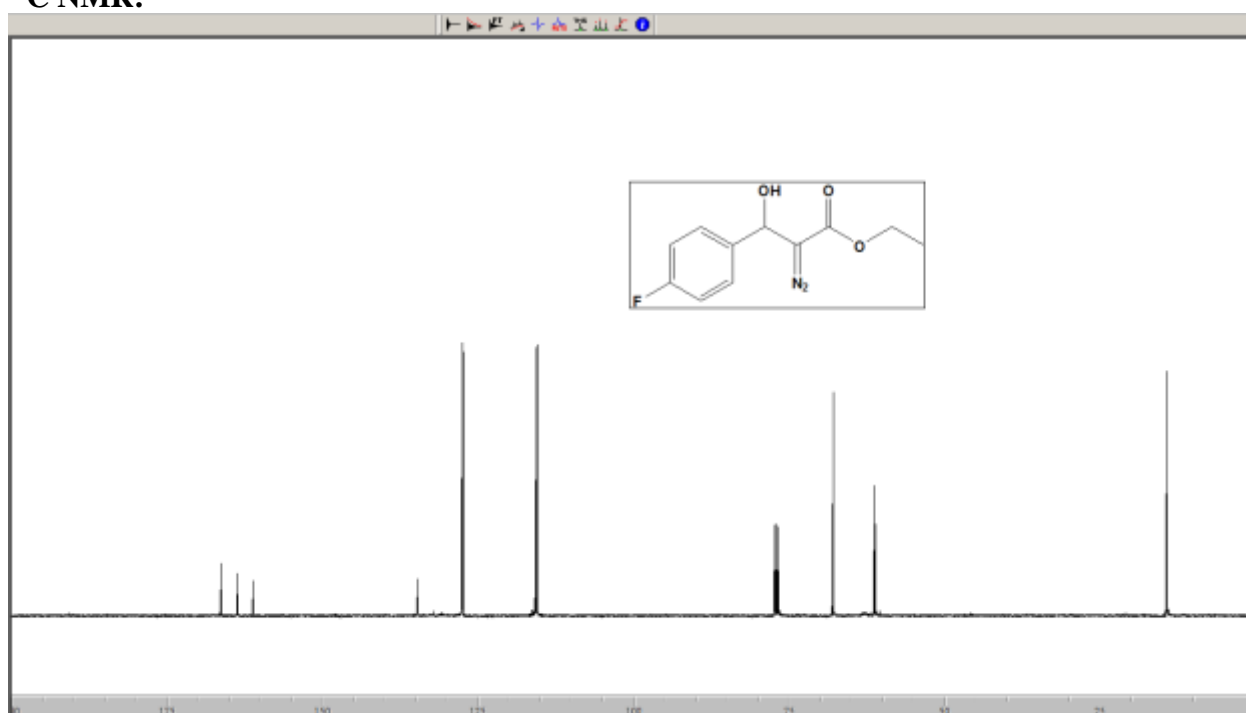


Ethyl 2-diazo-3-(4-fluorophenyl)-3-hydroxypropanoate (2d):^[4] Mass (EI): $m/z = 238$ (M^+); ^1H NMR (CDCl_3 , 400MHz) δ : 1.27 (t, $J = 7.07$ Hz, 3H), 3.61 (bs, 1H), 4.23 (q, $J = 7.07$ Hz, 2H), 5.89 (s, 1H), 7.04-7.08 (m, 2H), 7.38-7.42 (m, 2H) ; ^{13}C NMR (CDCl_3 , 100MHz) δ : 14.44, 61.31, 68.04, 115.55, 127.50, 134.87, 161.25, 163.70, 166.42.

^1H NMR:

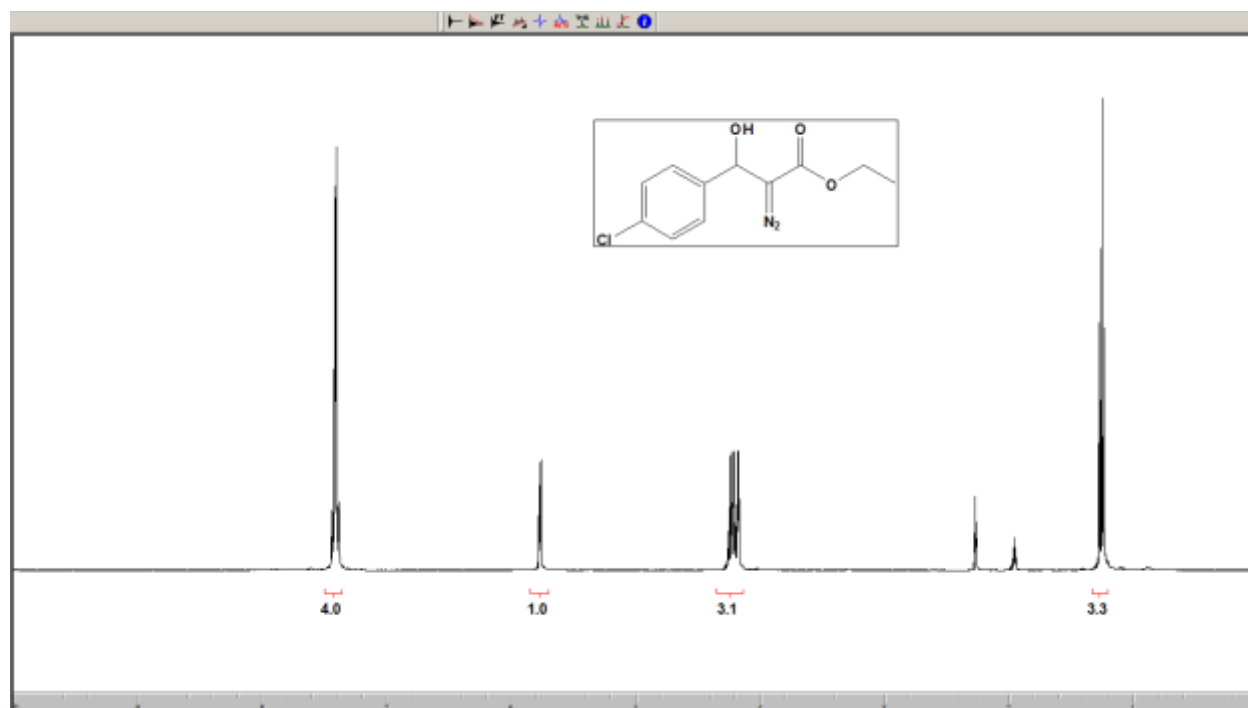


^{13}C NMR:

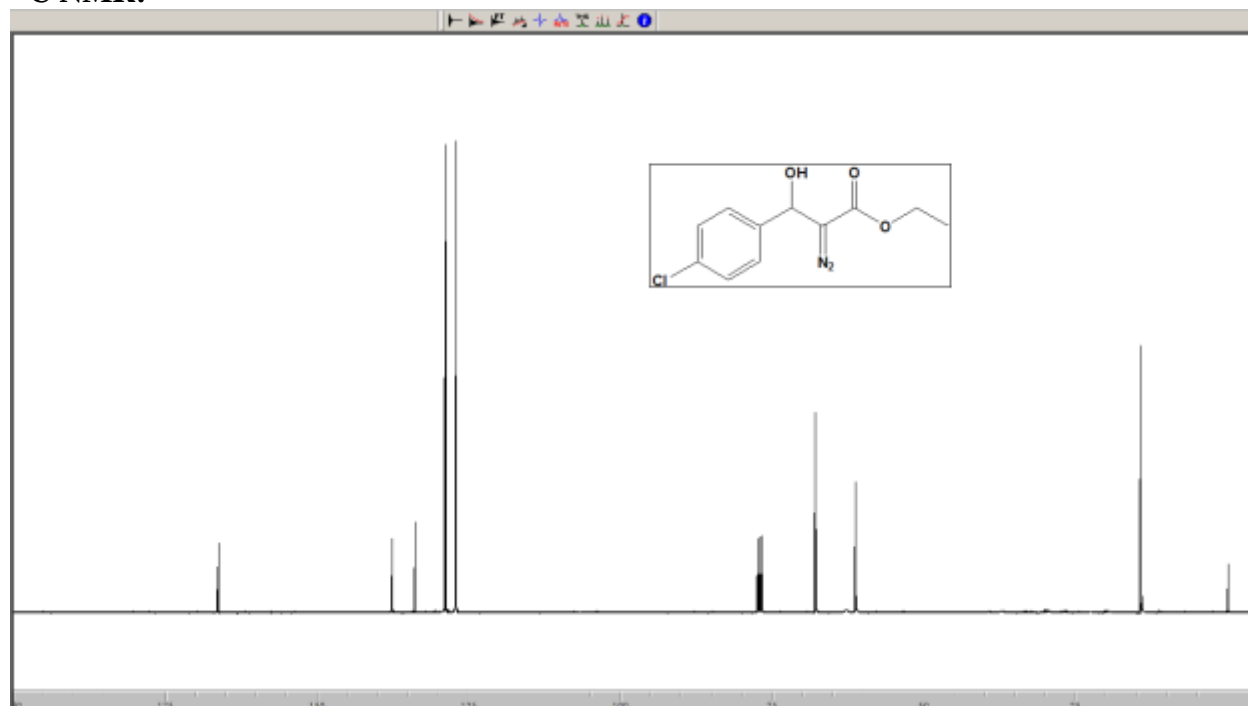


Ethyl 3-(4-chlorophenyl)-2-diazo-3-hydroxypropanoate (2e).^[3] Mass (EI): $m/z = 254$ (M^+); ^1H NMR (CD_3CN , 400MHz) δ : 1.26 (t, $J = 7.07$, 3H), 4.17- 4.26 (m, 3H), 5.77 (d, $J = 4.3\text{Hz}$, 1H), 7.38-7.44 (m, 4H); ^{13}C NMR (CDCl_3 , 100MHz) δ : 14.41, 61.34, 67.94, 127.15, 128.89, 133.97, 137.67, 166.36.

^1H NMR:

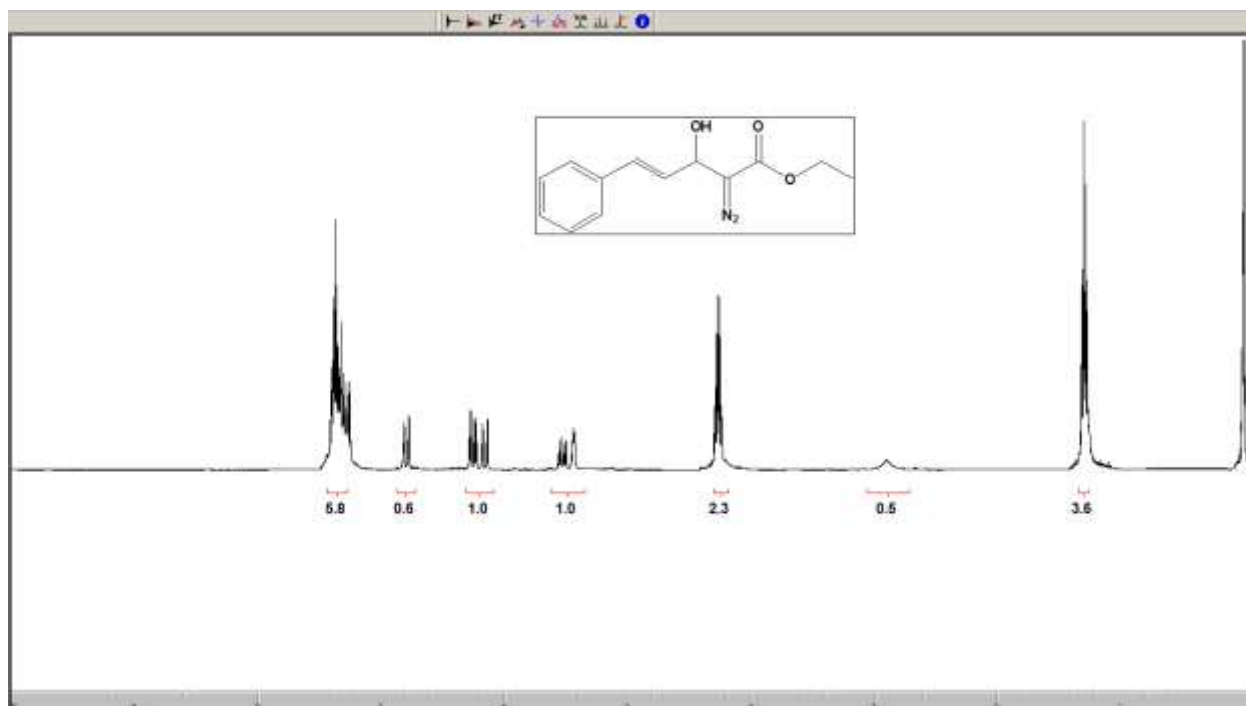


^{13}C NMR:

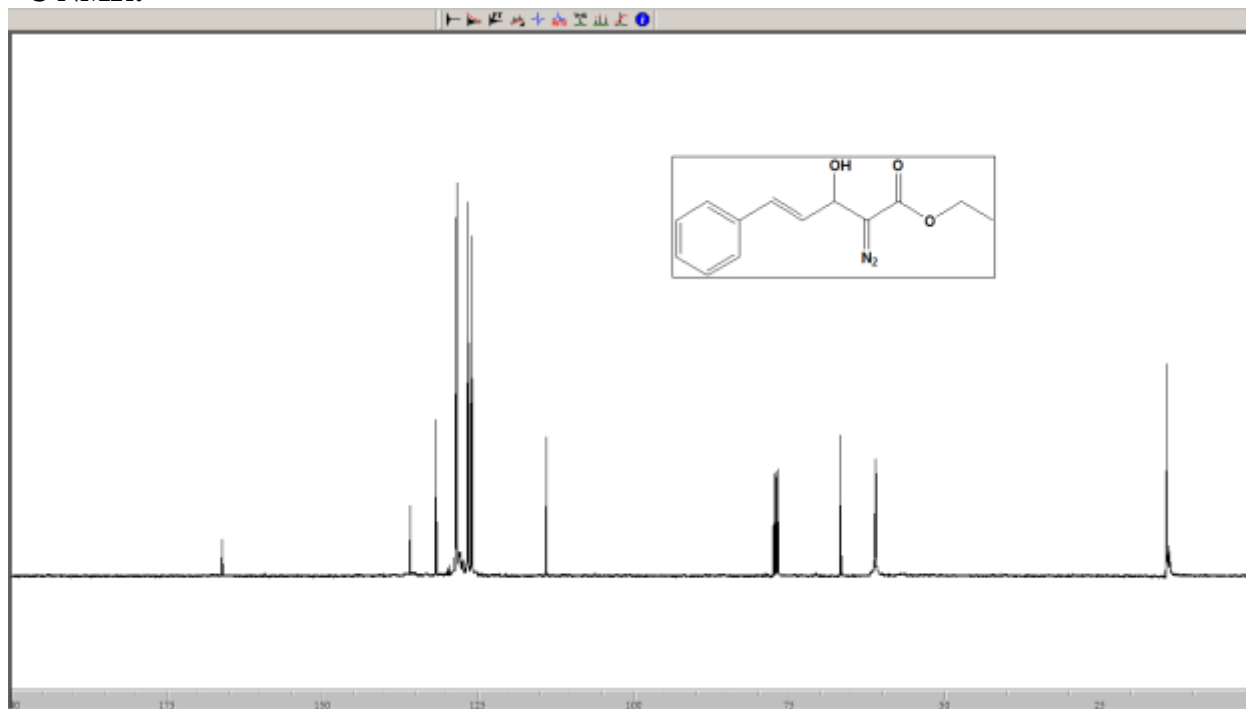


(E)-Ethyl 2-diazo-3-hydroxy-5-phenylpent-4-enoate (2f):^[2] Mass (EI): $m/z = 246$ (M^+); ^1H NMR (CDCl_3 , 400MHz) δ : 1.28 (t, $J = 7.07$, 3H), 2.90 (bs, 1H), 4.26 (q, $J = 7.07$ Hz, 2H), 5.44-5.54 (m, 1H), 6.14 (dd, $J = 15.9\text{Hz}$ & 5.4 Hz, 1H), 6.77 (d, $J = 15.9\text{Hz}$, 1H), 7.25-7.40 (m, 5H); ^{13}C NMR (CDCl_3 , 100MHz) δ : 14.41, 61.13, 66.77, 114.13, 126.13, 126.66, 128.52, 131.81, 135.00, 166.17.

^1H NMR:

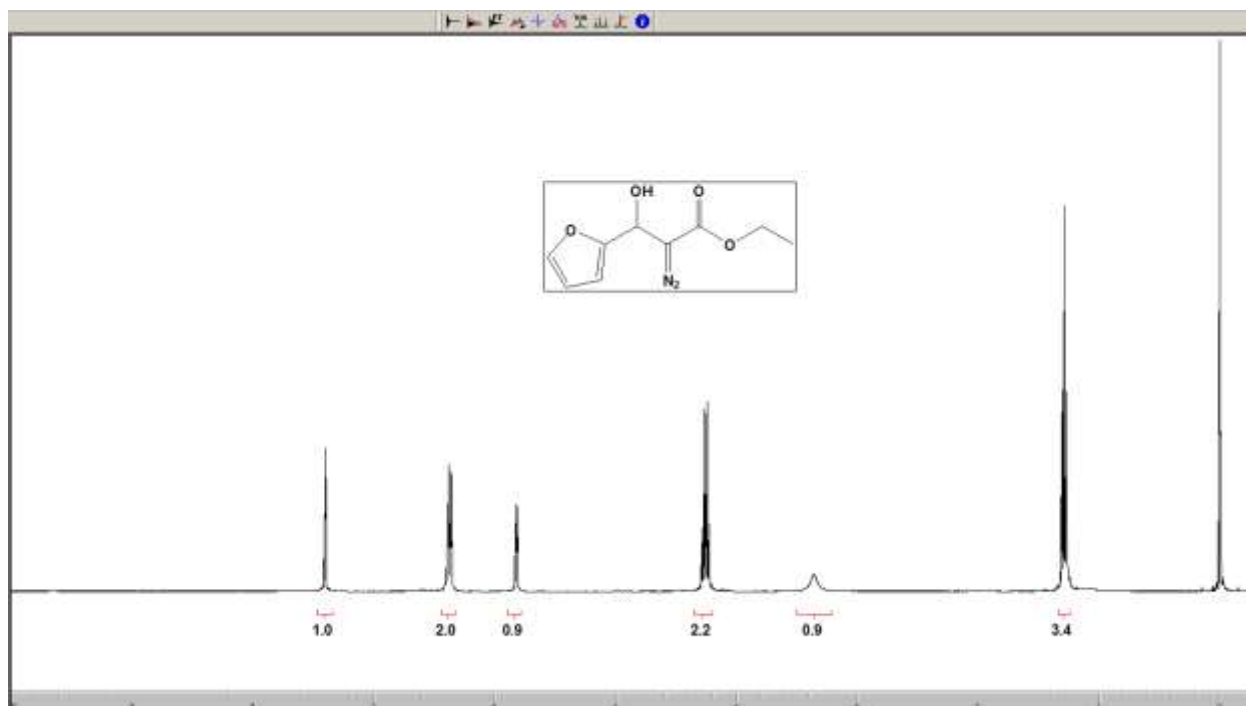


^{13}C NMR:

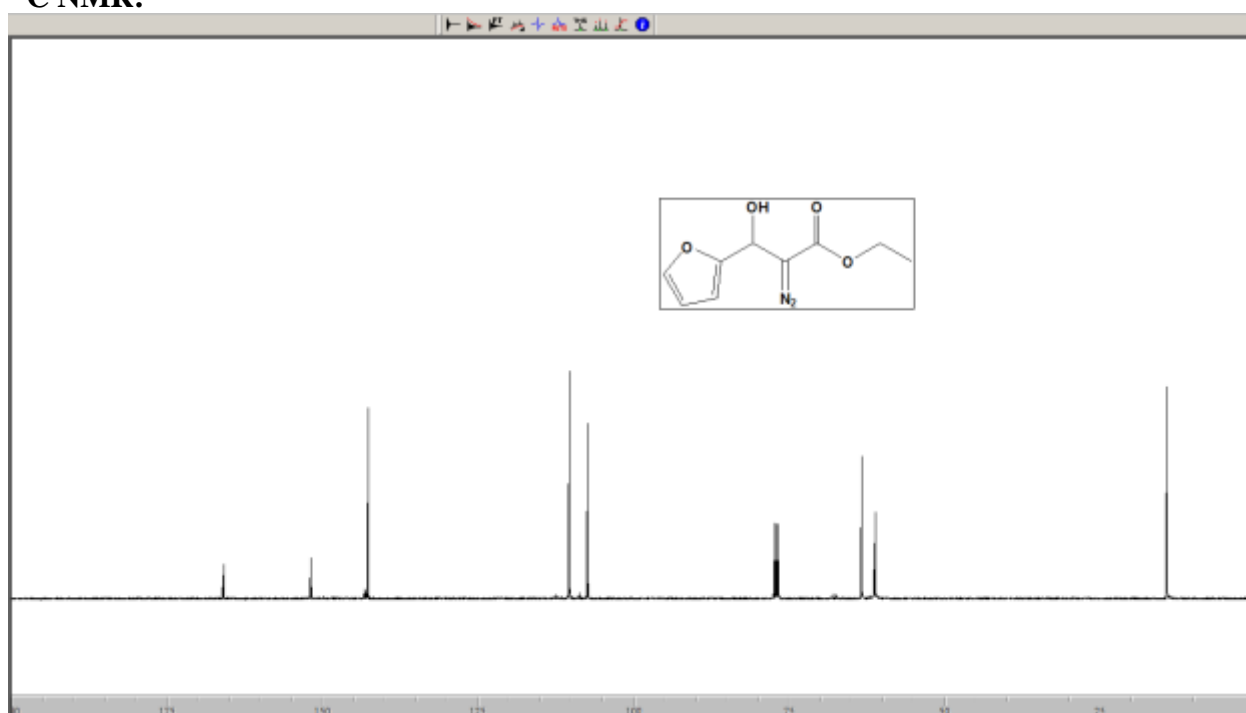


Ethyl 2-diazo-3-(furan-2-yl)-3-hydroxypropanoate (2g):^[2] Mass (ED): $m/z = 210 (M^+)$; ¹H NMR (CDCl₃, 400MHz) δ : 1.27 (t, J = 7.07 Hz, 3H), 3.36 (bs, 1H), 4.23 (q, J = 7.07Hz, 2H), 5.82 (s, 1H), 6.36-6.39 (m, 2H), 7.38-7.40 (m, 1H) ; ¹³C NMR (CDCl₃, 100MHz) δ : 14.43, 61.29, 63.43, 107.43, 110.41, 142.77, 151.92, 166.00.

¹H NMR:

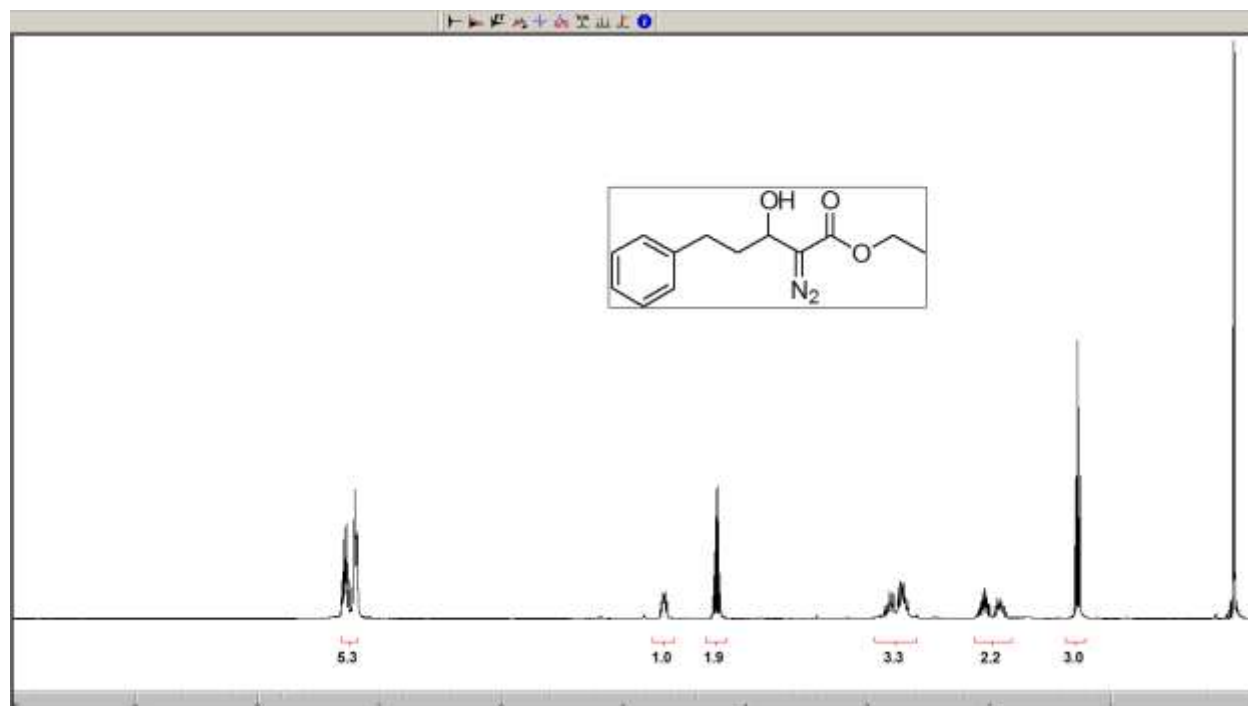


¹³C NMR:

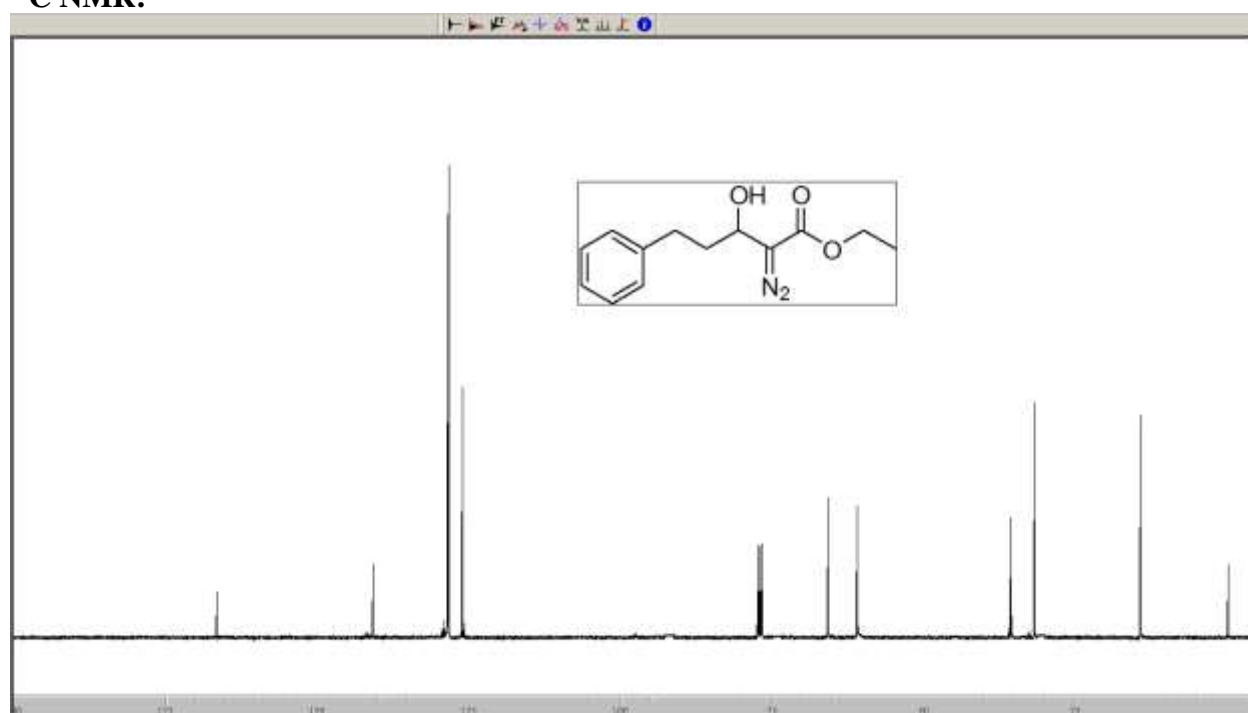


Ethyl 2-diazo-3-hydroxy-5-phenylpentanoate (2h):^[2] Mass (EI): $m/z = 248$ (M^+); ^1H NMR (CDCl_3 , 400MHz) δ : 1.26 (t, $J = 7.07$, 3H), 1.87-2.01 (m, 2H), 2.68-2.86 (m, 3H), 4.21 (q, $J = 7.07$ Hz, 2H), 4.65-4.70 (m, 1H), 7.17-7.31 (m, 5H); ^{13}C NMR (CDCl_3 , 100MHz) δ : 14.45, 31.89, 35.74, 61.06, 65.92, 126.12, 128.42, 140.90, 166.58.

^1H NMR:

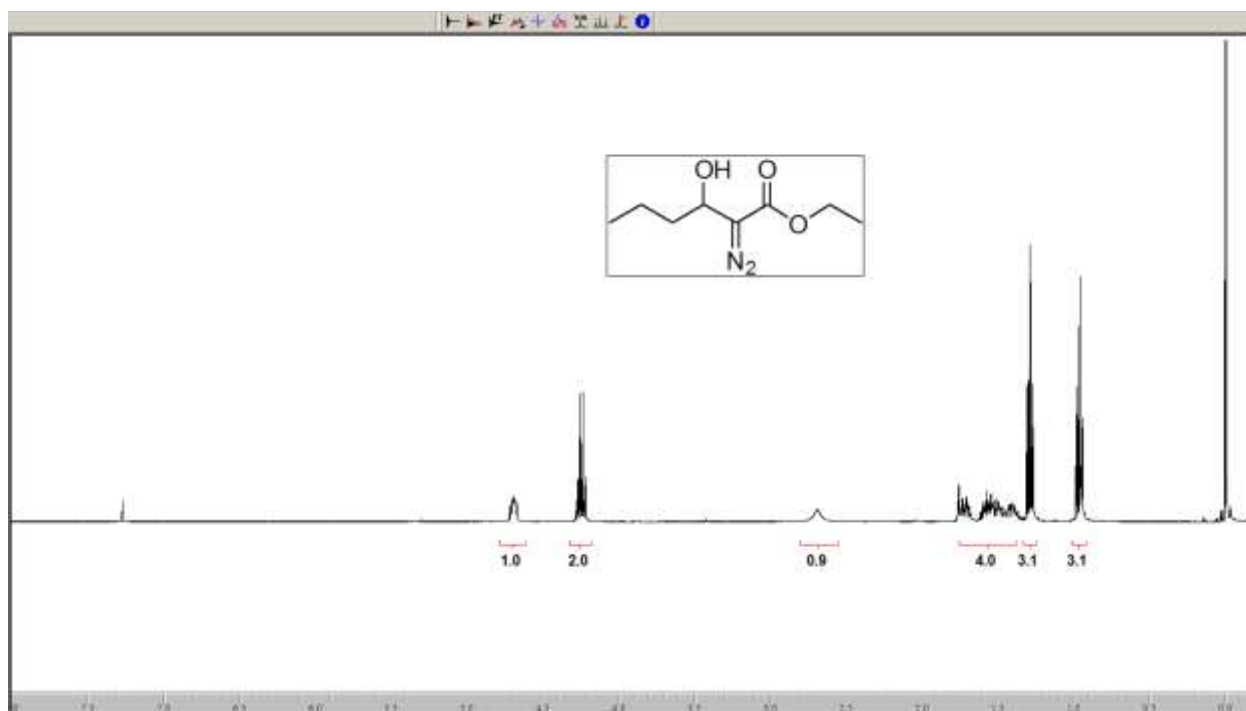


^{13}C NMR:

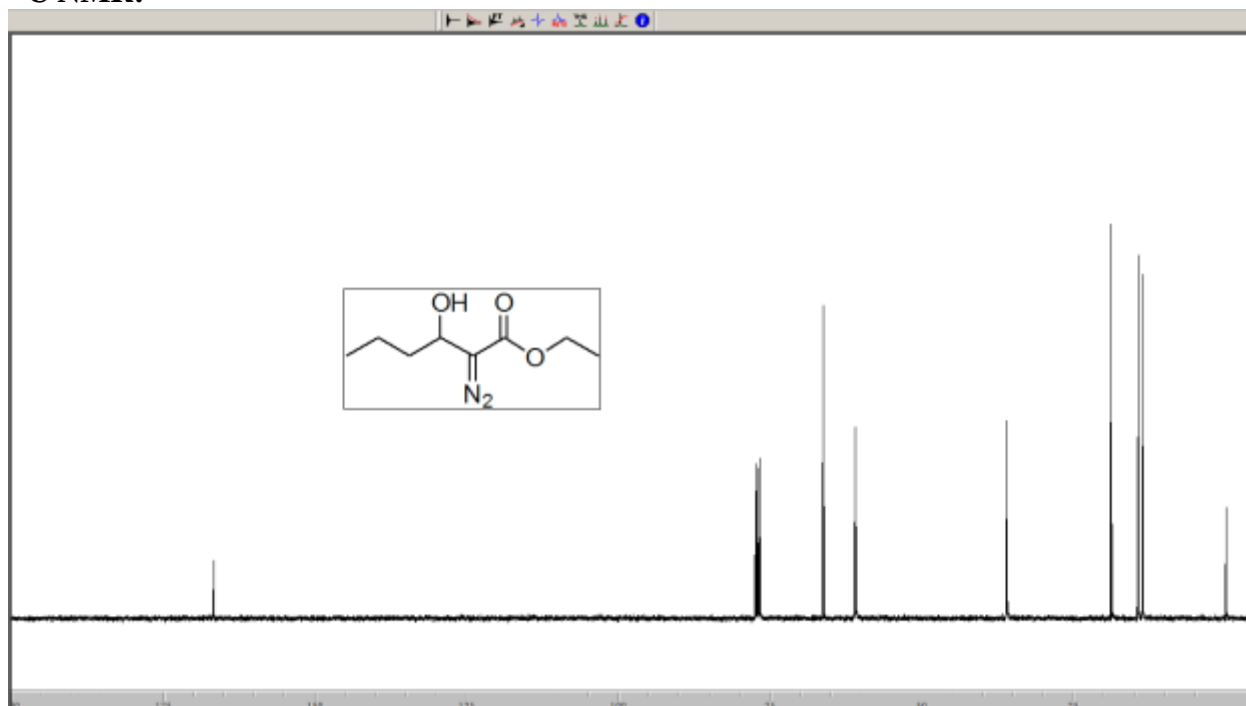


Ethyl 2-diazo-3-hydroxyhexanoate (2i):^[5] Mass (EI): $m/z = 186$ (M^+); ^1H NMR (CDCl_3 , 400MHz) δ : 0.95 (t, $J = 7.07$ Hz, 3H), 1.27 (t, $J = 7.07$, 3H), 1.37-1.73 (m, 4H), 2.70 (bs, 1H), 4.22 (q, $J = 7.07$ Hz, 2H), 4.67-4.72 (m, 1H); ^{13}C NMR (CDCl_3 , 100MHz) δ : 13.71, 14.47, 18.88, 36.08, 61.02, 66.28, 166.74.

^1H NMR:

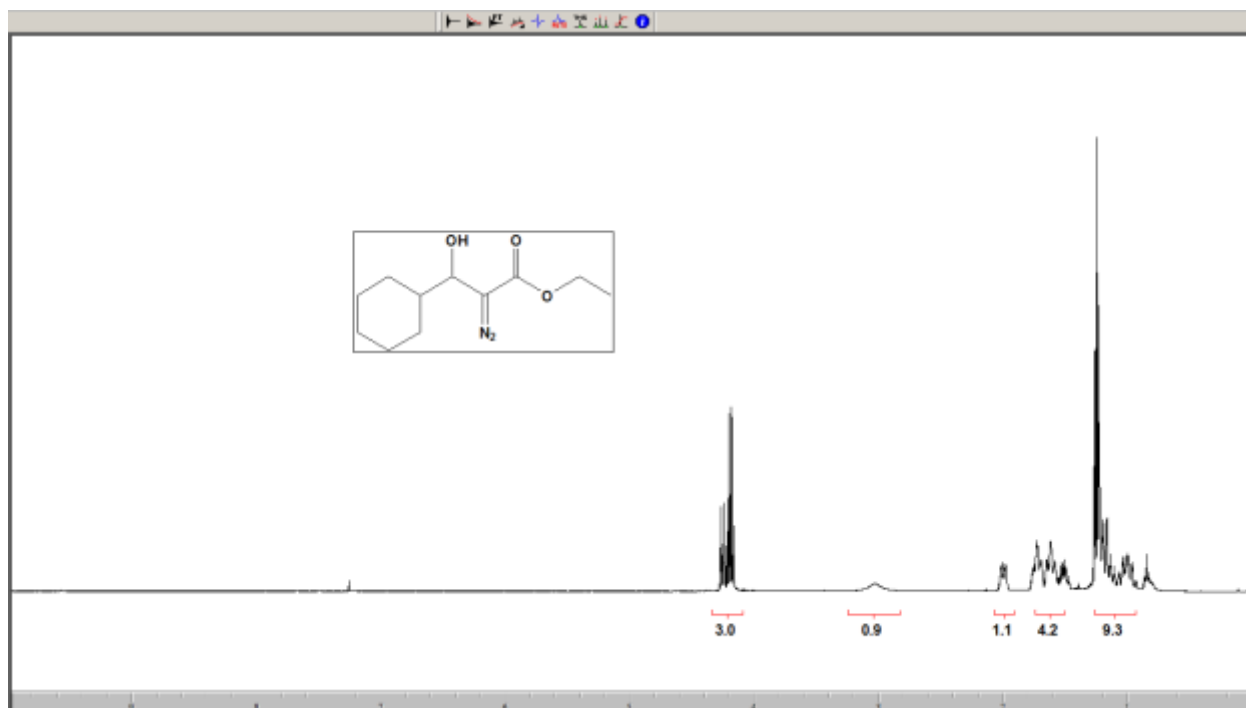


^{13}C NMR:

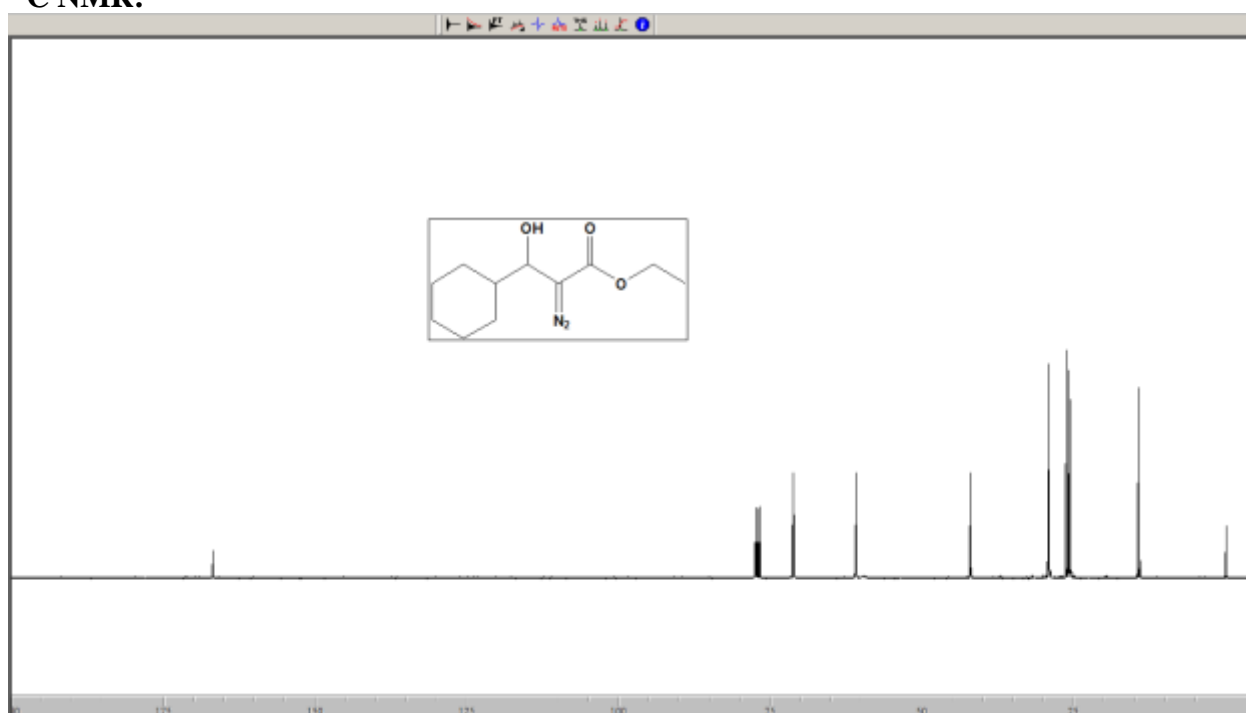


Ethyl 3-cyclohexyl-2-diazo-3-hydroxypropanoate (2j):^[4] Mass (EI): $m/z = 226$ (M^+); ^1H NMR (CDCl_3 , 400MHz) δ : 0.93-1.28 (m, 9H), 1.50-1.76 (m, 4H), 1.98-2.02 (m, 1H), 3.03 (bs, 1H), 4.17 (q, $J = 7.07\text{Hz}$, 2H), 4.25 (d, $J = 8.54\text{ Hz}$, 1H); ^{13}C NMR (CDCl_3 , 100MHz) δ : 14.46, 25.66, 26.27, 29.15, 42.08, 60.95, 71.25, 166.88.

^1H NMR:

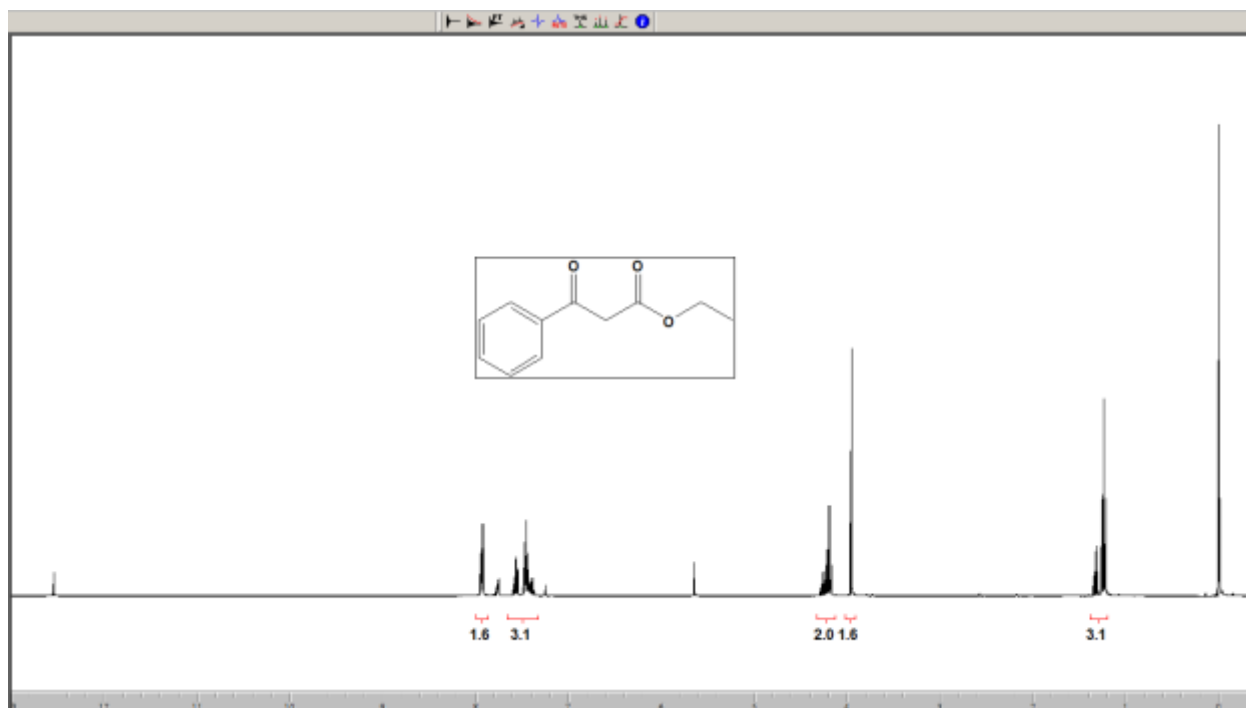


^{13}C NMR:

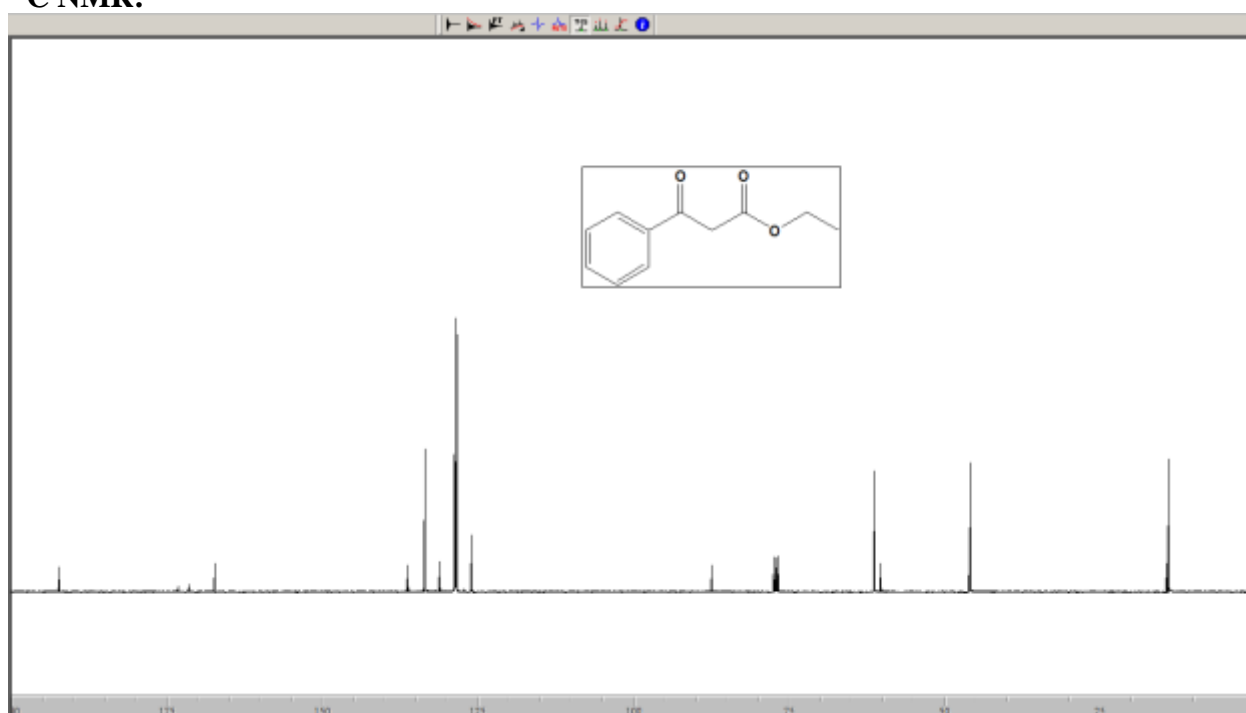


Ethyl 3-oxo-3-phenylpropanoate (3a):^[6] Mass (EI): $m/z = 192$ (M^+); ^1H NMR of major keto-form (CDCl_3 , 400MHz) δ : 1.22-1.26 (m, 3H), 3.96 (s, 2H), 4.17-4.29 (m, 2H), 7.37-7.48 (m, 2H), 7.55-7.59 (m, 1H), 7.92-7.95 (m, 2H); ^{13}C NMR (CDCl_3 , 100MHz) δ : 14.06, 46.02, 60.31, 61.39, 87.51, 126.12, 128.55, 128.80, 131.22, 133.63, 136.36, 167.41, 192.42.

^1H NMR:

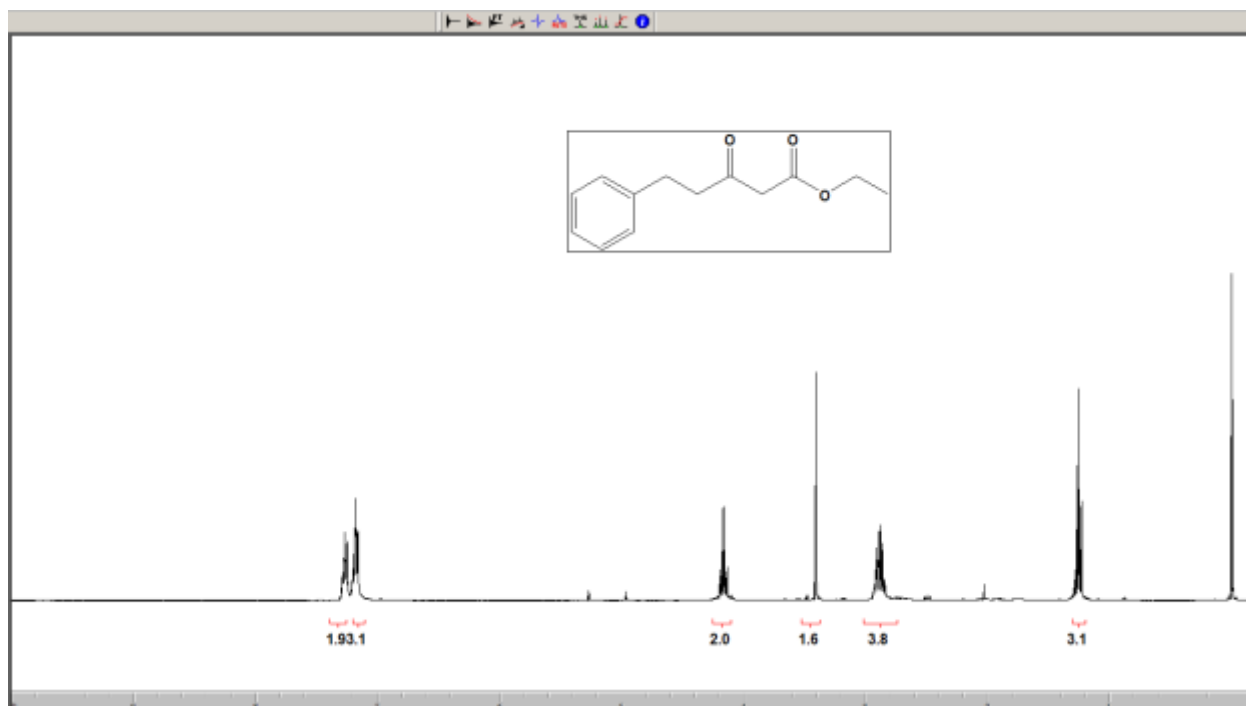


^{13}C NMR:

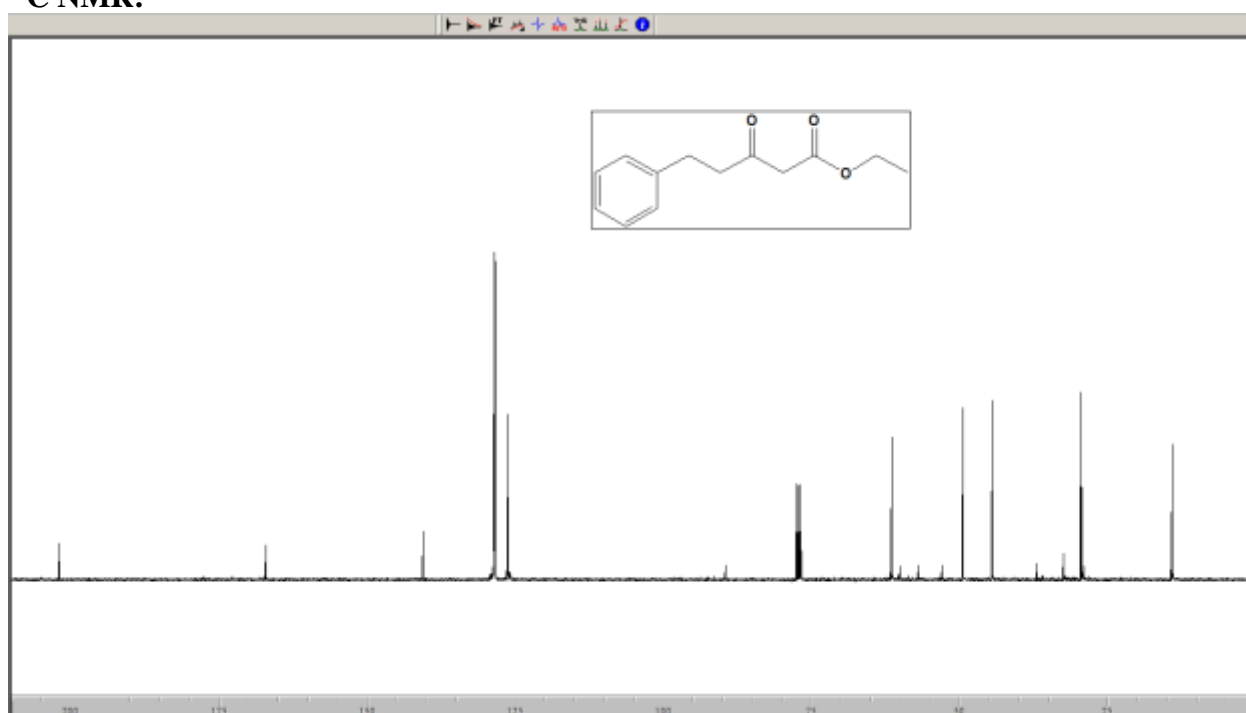


Ethyl 3-oxo-5-phenylpentanoate (3h):^[7] Mass (EI): $m/z = 220$ (M^+); ^1H NMR of major keto-form (CDCl_3 , 400MHz) δ : 1.25 (t, $J = 7.32$ Hz, 3H), 2.84-2.94 (m, 4H), 3.41 (s, 2H), 4.14 (q, $J = 7.32$ Hz, 2H), 7.16-7.21 (m, 3H), 7.24-7.32 (m, 2H); ^{13}C NMR (CDCl_3 , 100MHz) δ : 14.20, 29.53, 44.59, 49.54, 61.51, 126.33, 128.42, 128.64, 140.65, 167.21, 202.00.

^1H NMR:

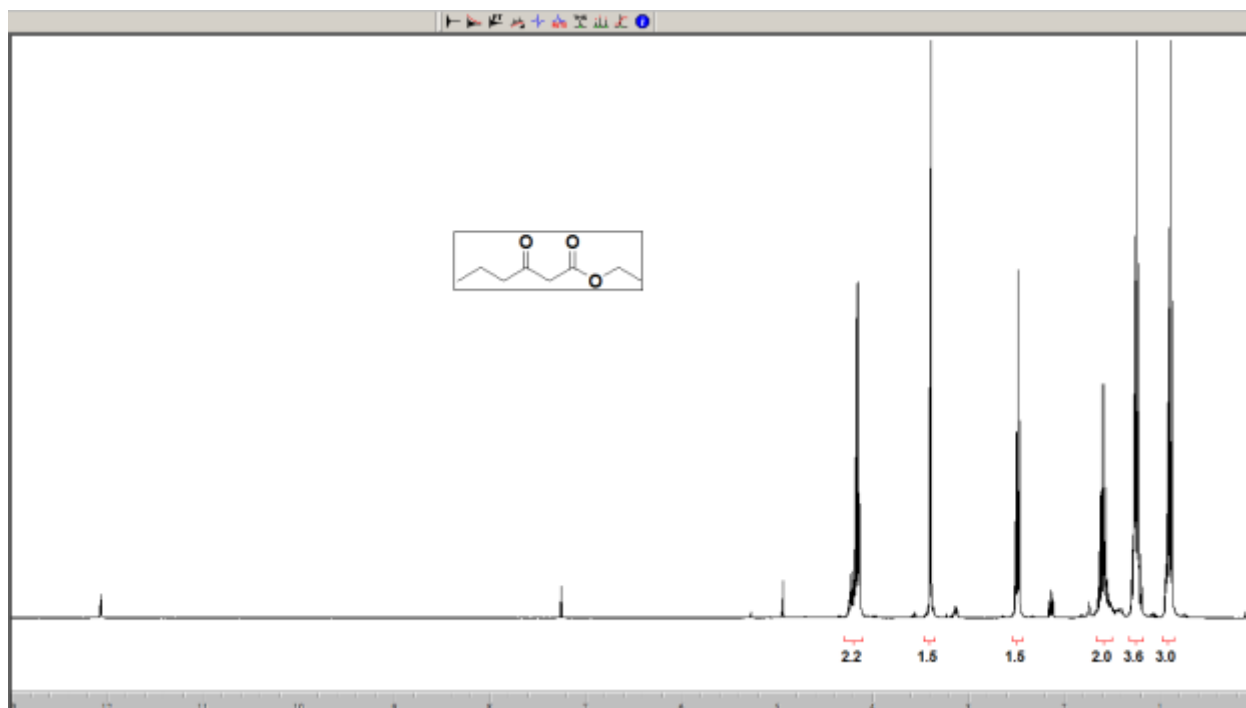


^{13}C NMR:

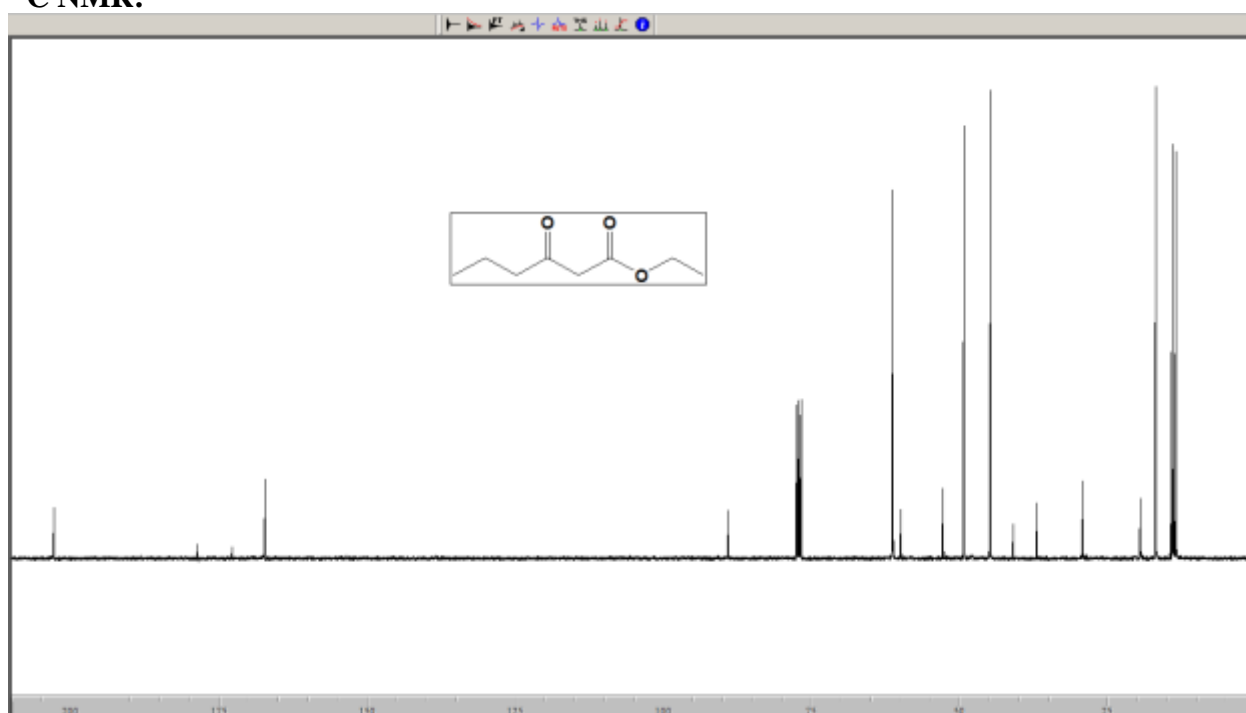


Ethyl 3-oxohexanoate (3i):^[8] Mass (EI): $m/z = 158$ (M^+); ^1H NMR of major keto-form (CDCl_3 , 400MHz) δ : 0.88 (t, $J = 7.32$ Hz, 3H), 1.23 (t, $J = 7.32$ Hz, 3H), 1.46-1.68 (m, 2H), 2.48 (t, $J = 7.07$ Hz, 2H), 3.40 (s, 2H), 4.13-4.23 (m, 2H); ^{13}C NMR (CDCl_3 , 100MHz) δ : 13.56, 14.12, 16.95, 19.63, 29.25, 40.98, 44.90, 49.34, 52.83, 59.92, 61.32, 89.13, 167.30, 172.80, 178.75, 202.90.

^1H NMR:

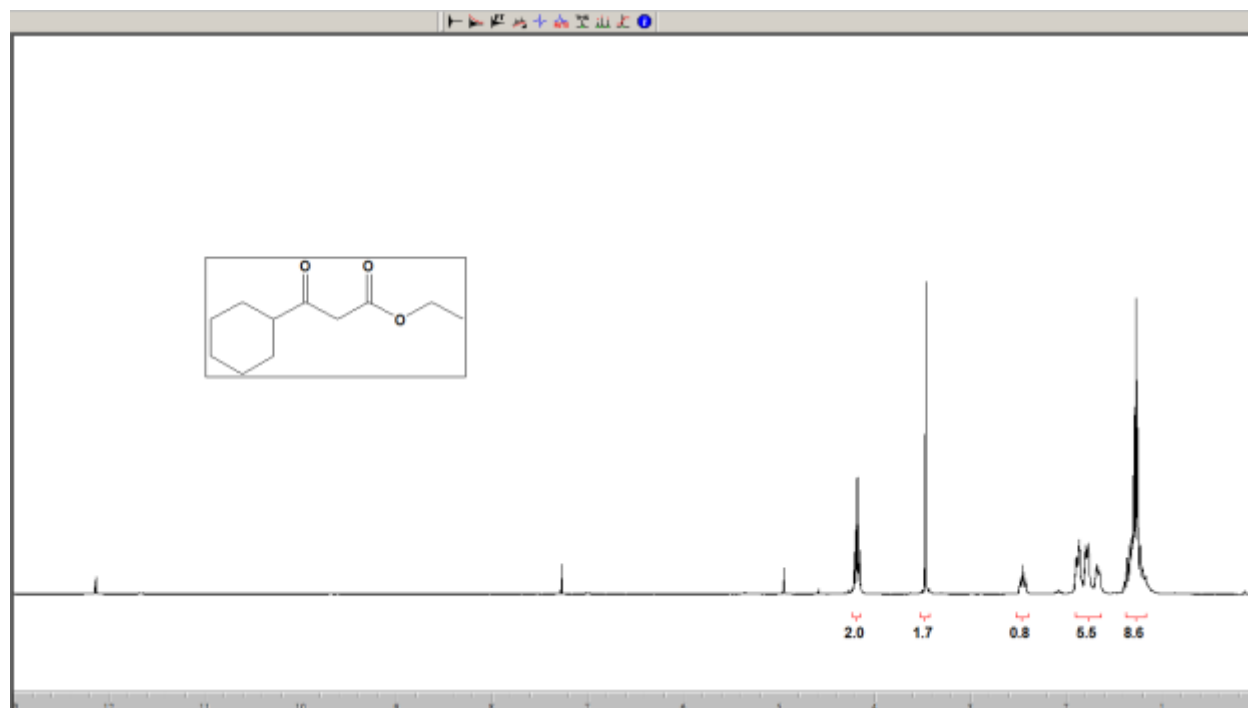


^{13}C NMR:

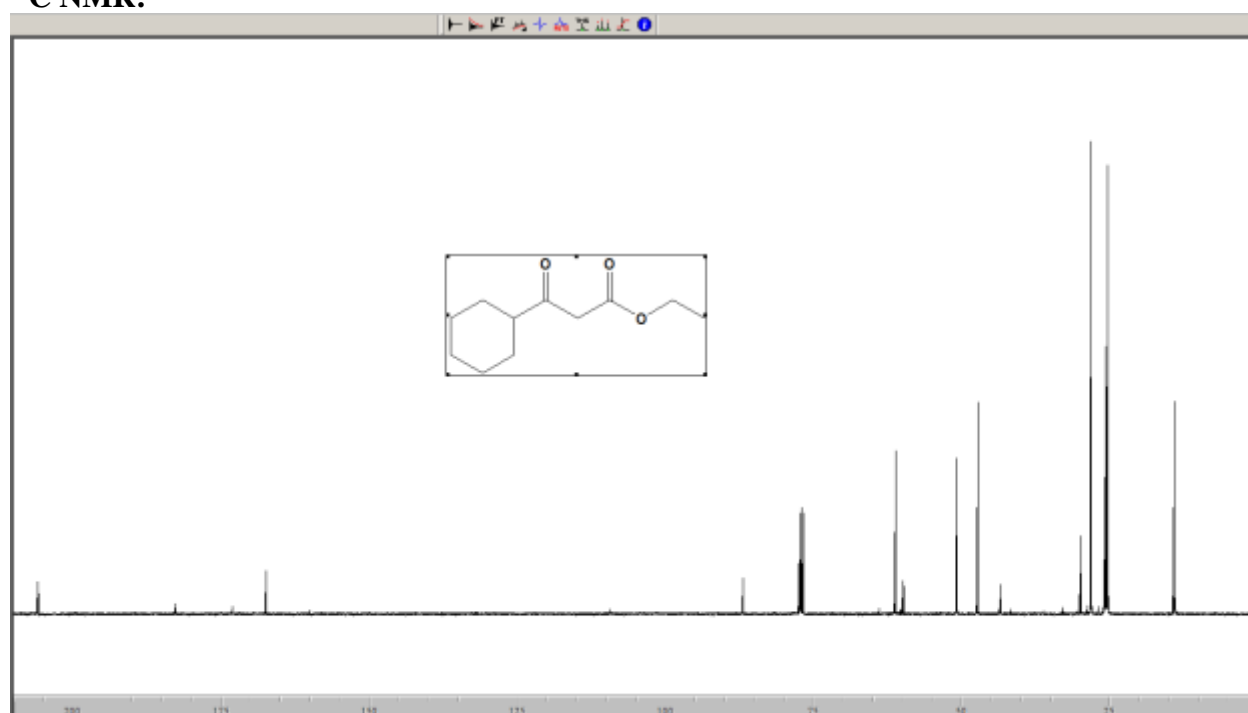


Ethyl 3-cyclohexyl-3-oxopropanoate (3j):^[9] Mass (EI): $m/z = 198$ (M^+); ^1H NMR of major keto-form (CDCl_3 , 400MHz) δ : 1.17-1.40 (m, 8H), 1.65-1.90 (m, 5H), 2.42-2.50 (m, 1H), 3.48 (s, 2H), 4.17 (q, $J = 7.2$ Hz, 2H); ^{13}C NMR (CDCl_3 , 100MHz) δ : 14.13, 14.30, 25.50, 25.75, 28.20, 29.99, 43.55, 47.37, 50.88, 59.90, 61.25, 86.98, 167.49, 173.14, 182.78, 205.92.

^1H NMR:

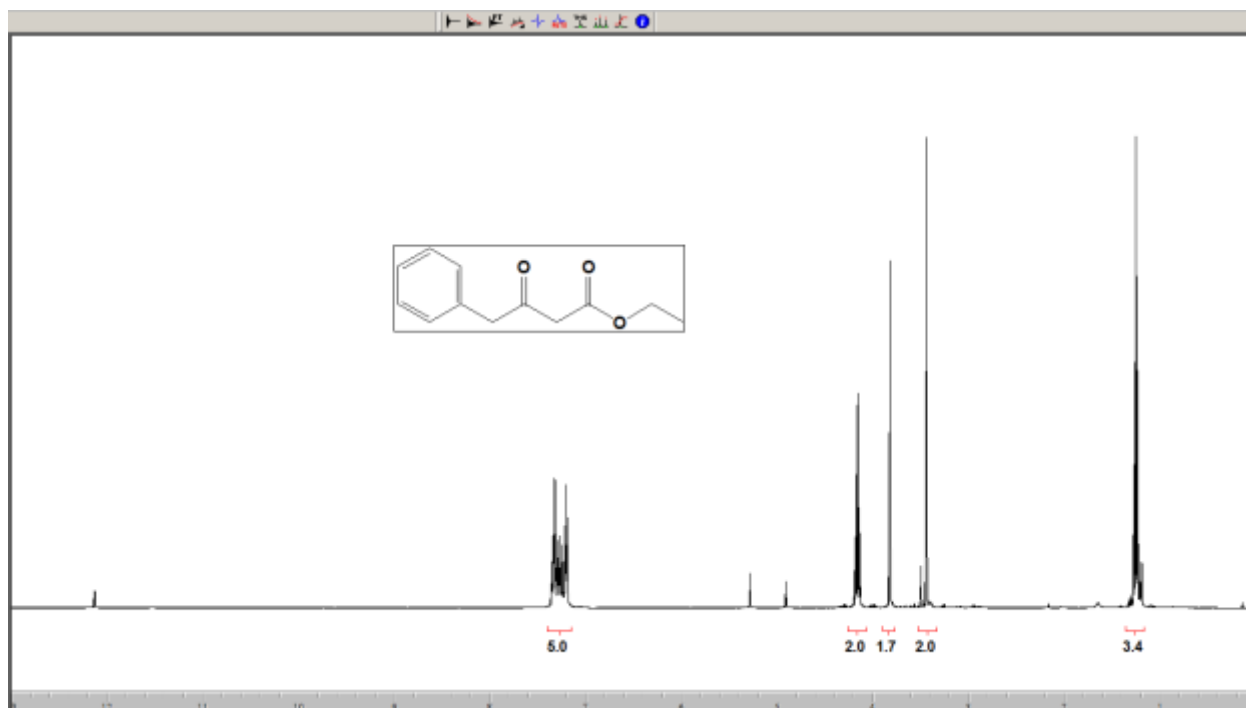


^{13}C NMR:

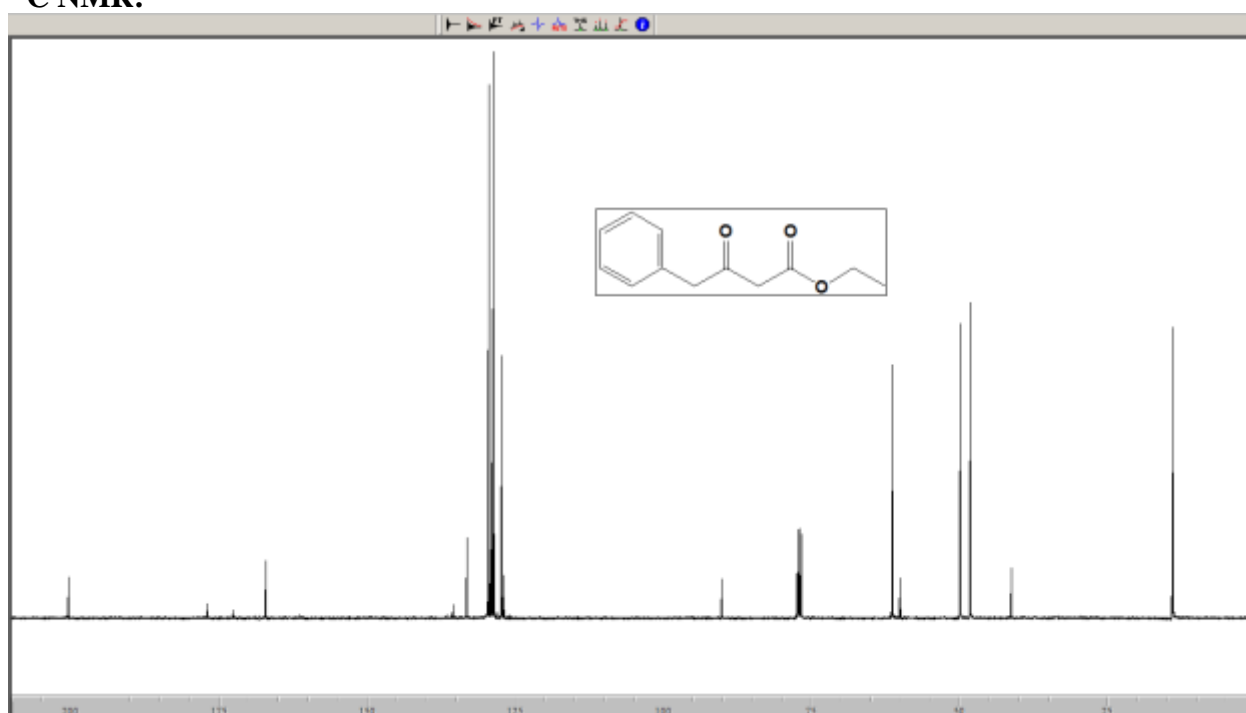


Ethyl 3-oxo-4-phenylbutanoate (3k):^[10] Mass (EI): $m/z = 206 (M^+)$; ^1H NMR of major keto-form (CDCl_3 , 400MHz) δ : 1.19-1.27 (m, 3H), 3.44 (s, 2H), 3.83 (s, 2H), 4.14-4.22 (m, 2H), 7.19-7.38 (m, 5H); ^{13}C NMR (CDCl_3 , 100MHz) δ : 14.07, 41.38, 48.28, 49.99, 60.07, 61.38, 90.19, 127.33, 128.82, 129.57, 133.24, 167.09, 172.62, 177.04, 200.50.

^1H NMR:

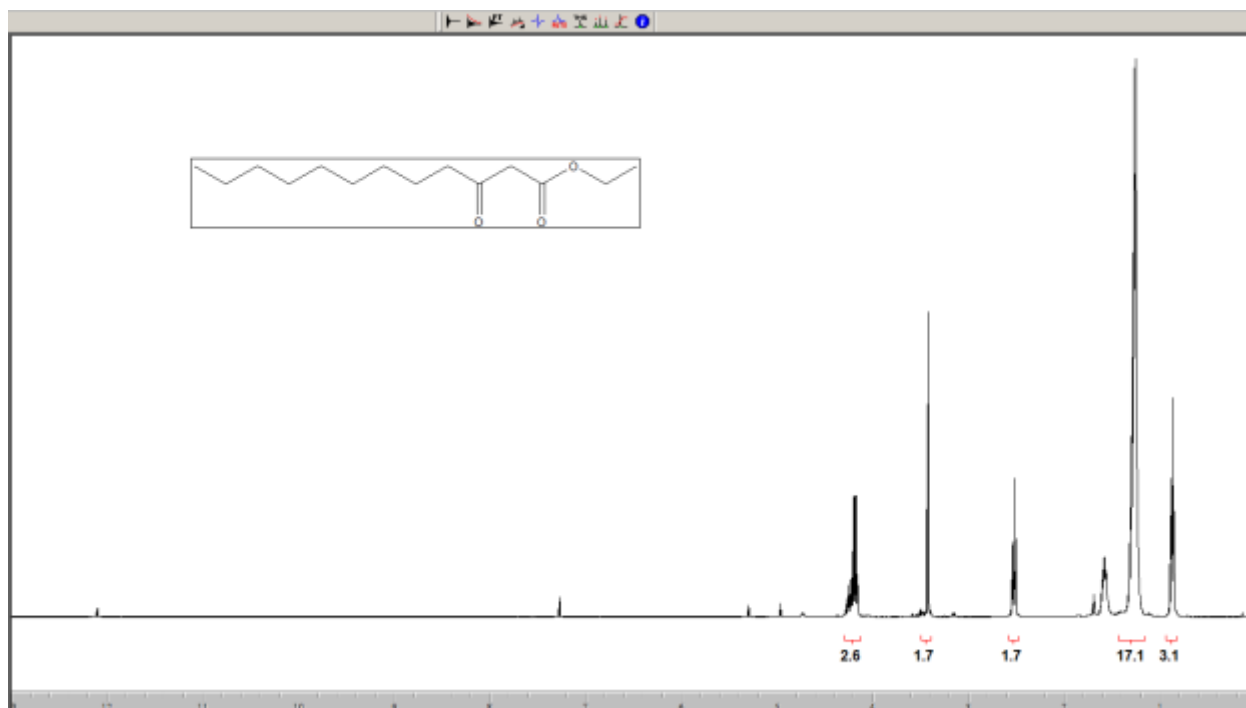


^{13}C NMR:

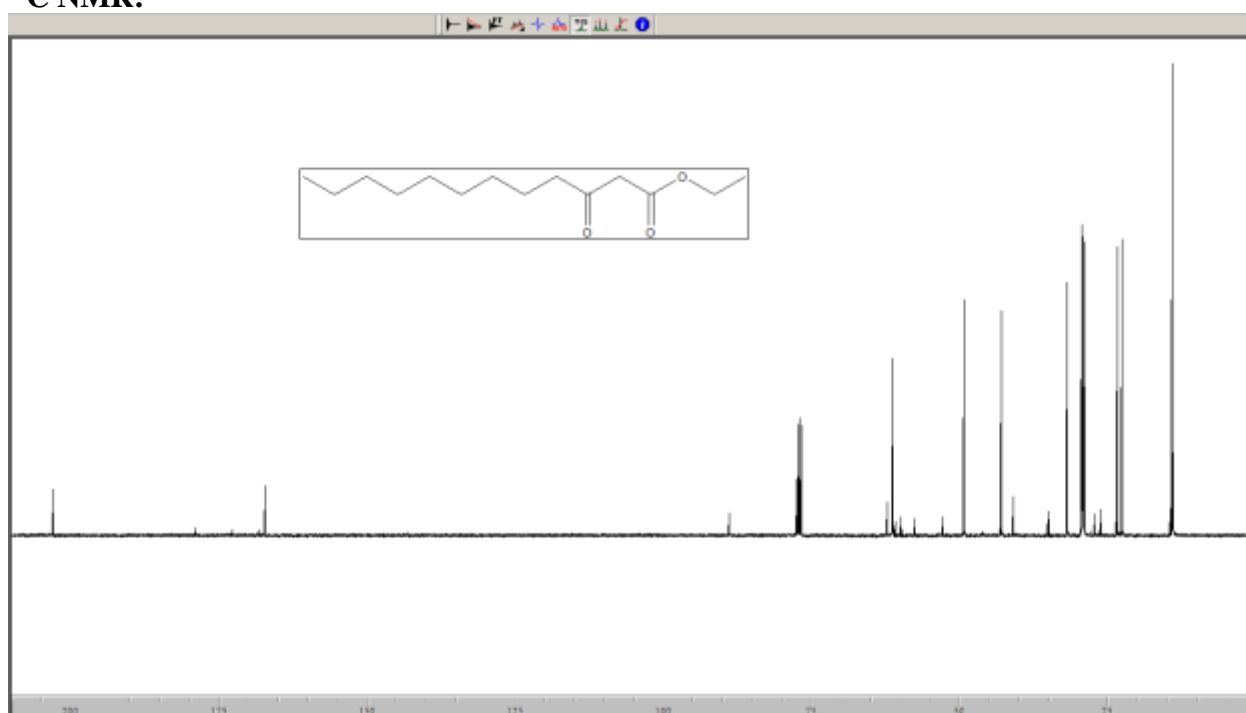


Ethyl 3-oxododecanoate (3l):^[11] Mass (EI): $m/z = 242$ (M^+); ^1H NMR of major keto-form (CDCl_3 , 400MHz) δ : 0.85-0.89 (m, 3H), 1.20-1.37 (M, 17H), 2.51 (t, $J = 7.32$ Hz, 2H), 3.43 (s, 2H), 4.16-4.28 (m, 2H); ^{13}C NMR (CDCl_3 , 100MHz) δ : 14.13, 22.70, 23.50, 29.05, 29.44, 31.89, 43.06, 49.33, 61.32, 88.97, 167.30, 172.81, 179.06, 203.02.

^1H NMR:



^{13}C NMR:



Reference:

- [1] K.-I. Min, T.-H. Lee, C. P. Park, Z.-Y. Wu, H. H. Girault, I. Ryu, T. Fukuyama, Y. Mukai, D.-P. Kim, *Angew. Chem. Int. Ed.* **2010**, *49*, 7063-7067.
- [2] B. M. Trost, S. Malhotra, B. A. Fried, *J. Am. Chem. Soc.* **2009**, *131*, 1674–1675.
- [3] M. L. Kantam, V. Balasubrahmanyam, K. B. S. Kumar, G. T. Venkanna, F. Figueras, *Adv. Synth. Catal.* **2007**, *349*, 1887 -1890.
- [4] P. R. Likhari, S. Roy, M. Roy, M. S. Subhas, M. L. Kantam, *Catal. Commun.* **2009**, *10*, 728-731.
- [5] W. Yao, J. Wang, *Org. Lett.* **2003**, *5*, 1527-1530.
- [6] C. D. F. Milagre, H. M. S. Milagre, P. J. S. Moran, J. A. R. Rodrigues, *J. Org. Chem.* **2010**, *75*, 1410-1418
- [7] J. S. Yadav, B. V. S. Reddy, K. V. Purnima, S. Jhansi, K. Nagaiah, N. Lingaiah, *Catal. Commun.* **2008**, *9*, 2361–2364.
- [8] B.S. Balaji, B. M. Chanda, *Tetrahedron*, **1998**, *54*, 13237-13252.
- [9] T. Misaki, R. Nagase, K. Matsumoto, Y. Tanabe, *J. Am. Chem. Soc.* **2005**, *127*, 2854–2855.
- [10] G. Sun, C. J. Fecko, R. B. Nicewonger, W. W. Webb, T. P. Begley, *Org. Lett.* **2006**, *8*, 681–683.
- [11] G. Doleschall, *Tetrahedron Lett.* **1988**, *48*, 6339-6340.