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Supplementary Material

Regioselective addition of 1,3-dicarbonyl dianions to carbonyl compounds: one pot lactonization and ketalization of *δ*-hydroxyl-*β*-keto esters to protected pyrone derivatives

Manas K. Ghorai*, Sandipan Halder and Sauvik Samanta

Department of Chemistry, Indian Institute of Technology, Kanpur, 208016, India
*Email: *mkghorai@iitk.ac.in*

1. General Information

Analytical thin layer chromatography (TLC) was carried out using silica gel 60 F_{254} pre-coated plates. Visualization was accomplished with UV lamp or I_2 stain. Silica gel 230-400 mesh size was used for flash column chromatography using the combination of ethyl acetate and petroleum ether as eluent. Unless noted, all reactions were carried out in oven-dried glassware under an atmosphere of nitrogen/argon using anhydrous solvents. Where appropriate, all reagents were purified prior to use following the guidelines of Perrin and Armarego.[1] All commercial reagents were used as received. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded at 400 MHz/500 MHz. Chemical shifts were recorded in parts per million (ppm, δ) relative to tetramethyl silane (δ 0.00). ^{1}H NMR splitting patterns are designated as singlet (s), doublet (d), doublet of doublet (dd), triplet (t), quartet (q), multiplet (m). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded at 100 MHz/125 MHz. Mass spectra (MS) were obtained using ESI mass spectrometers. IR spectra were recorded as neat for liquid and in KBr for solids. Melting points were determined using a hot stage apparatus and were uncorrected. Optical rotations were measured using a 2.0 mL cell with a 1.0 dm path length and are reported as $[\alpha]^{25}_{D}$ (*c* in g per 100 mL solvent) at 25 °C.

2. Selected NMR spectra

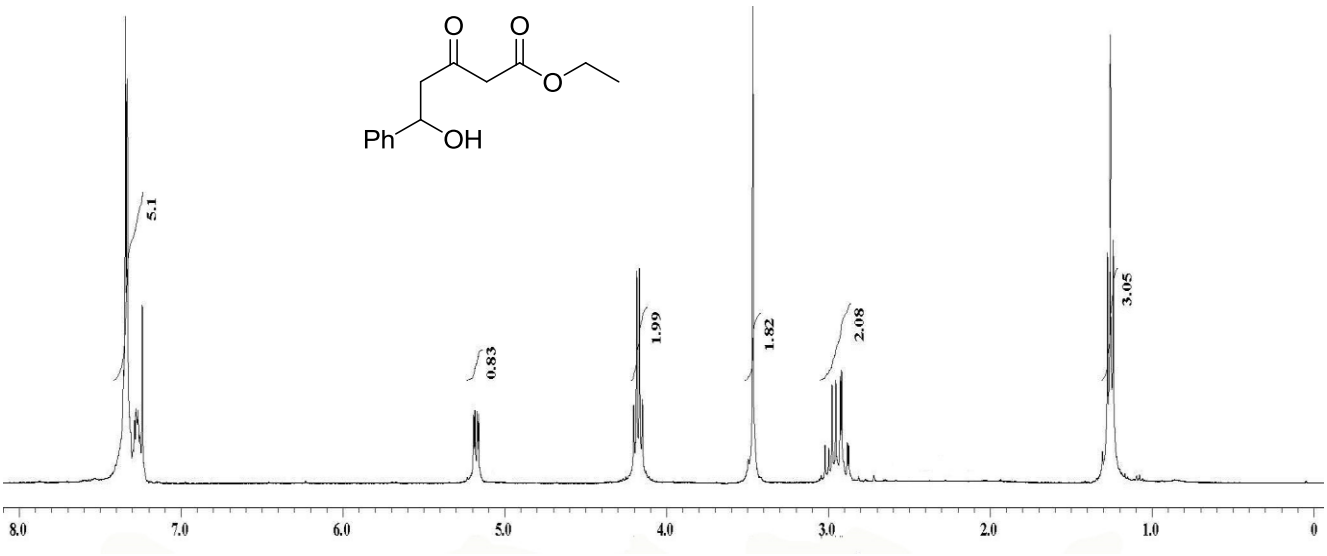

Figure 1: ^{1}H NMR spectrum of **4a** ($CDCl_3$, 500 MHz)

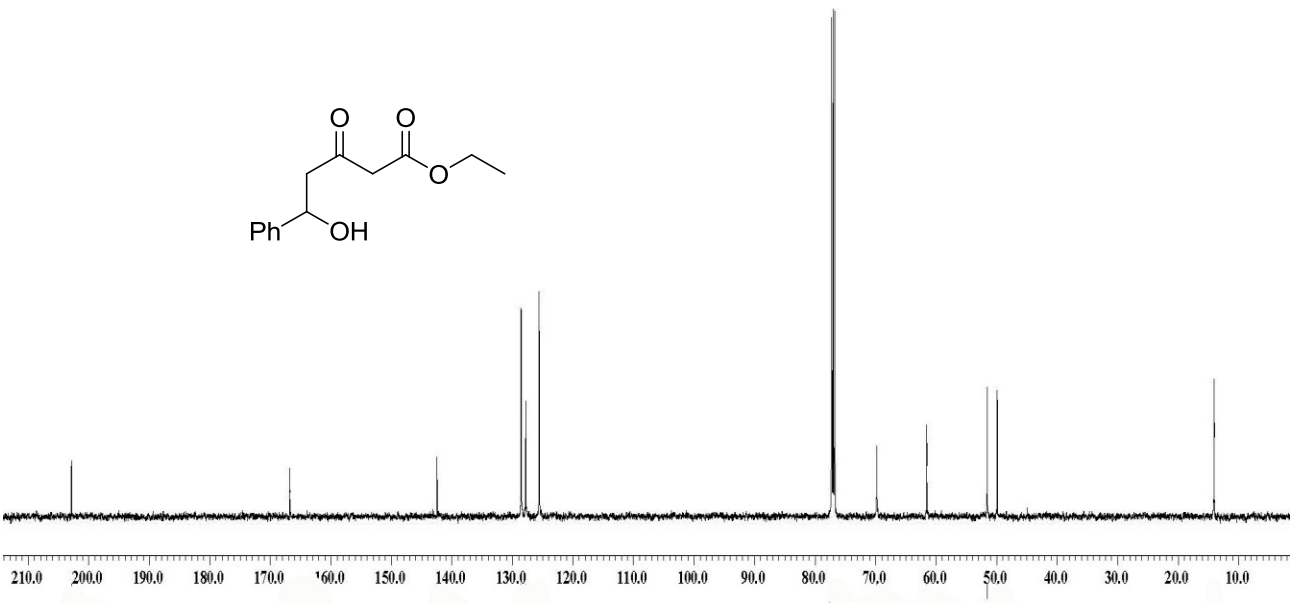

Figure 2: ^{13}C NMR spectrum of **4a** ($CDCl_3$, 125 MHz)

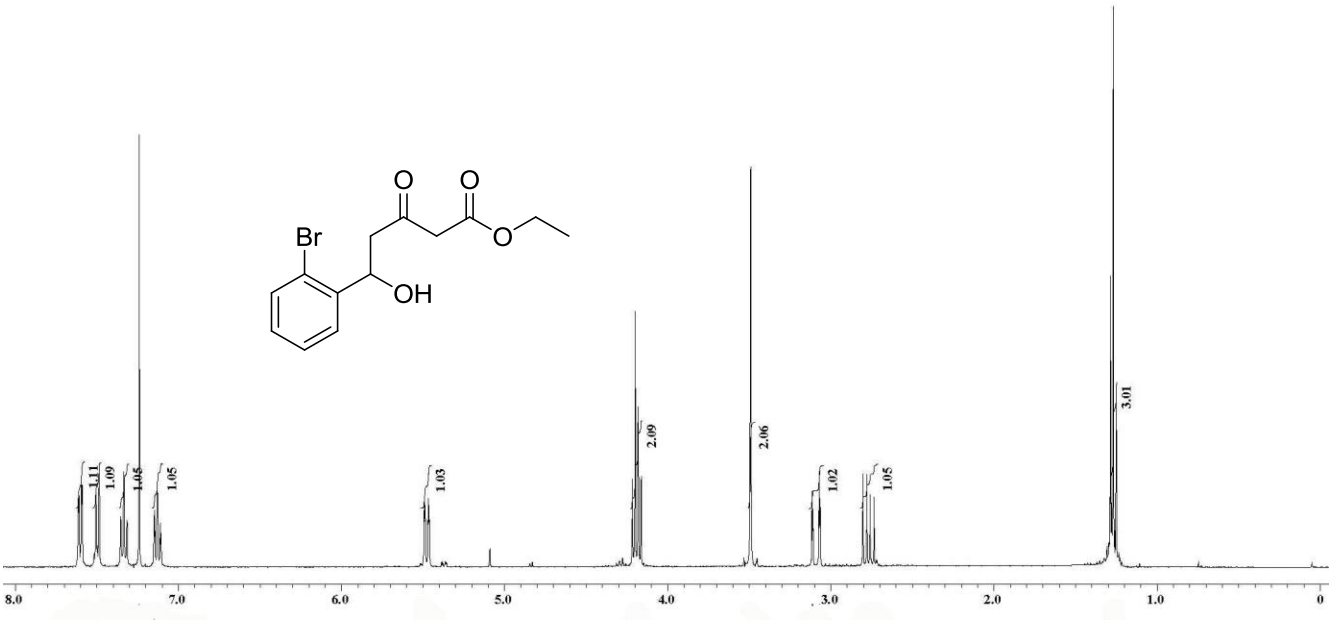

Figure 3: ^{1}H NMR spectrum of **4b** ($CDCl_3$, 400 MHz)

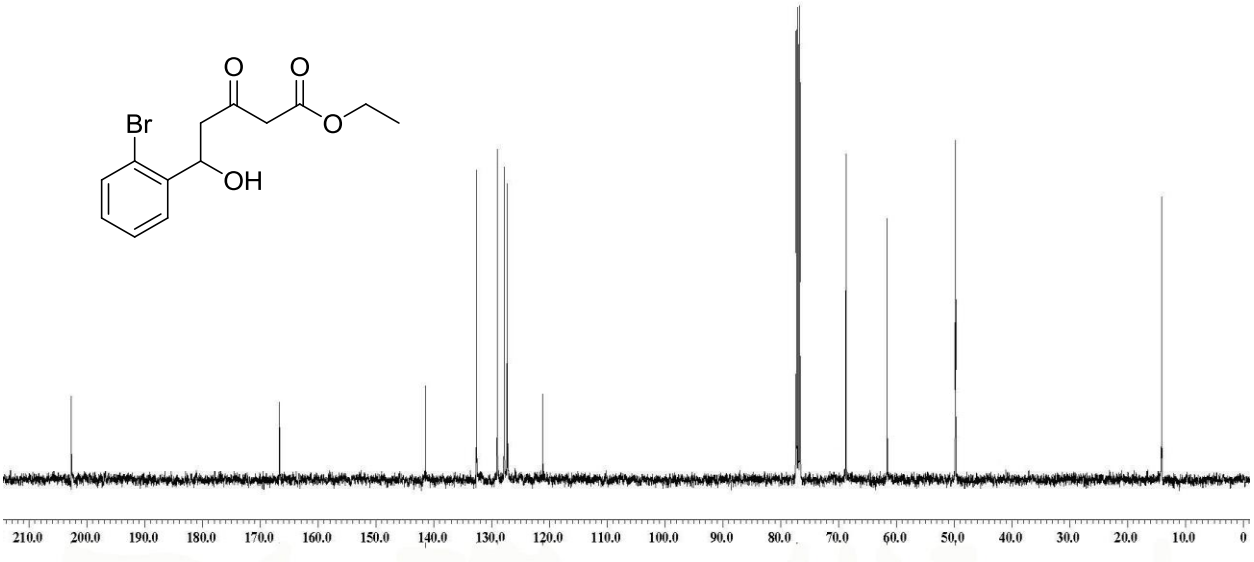

Figure 4: ^{13}C NMR spectrum of **4b** ($CDCl_3$, 100 MHz)

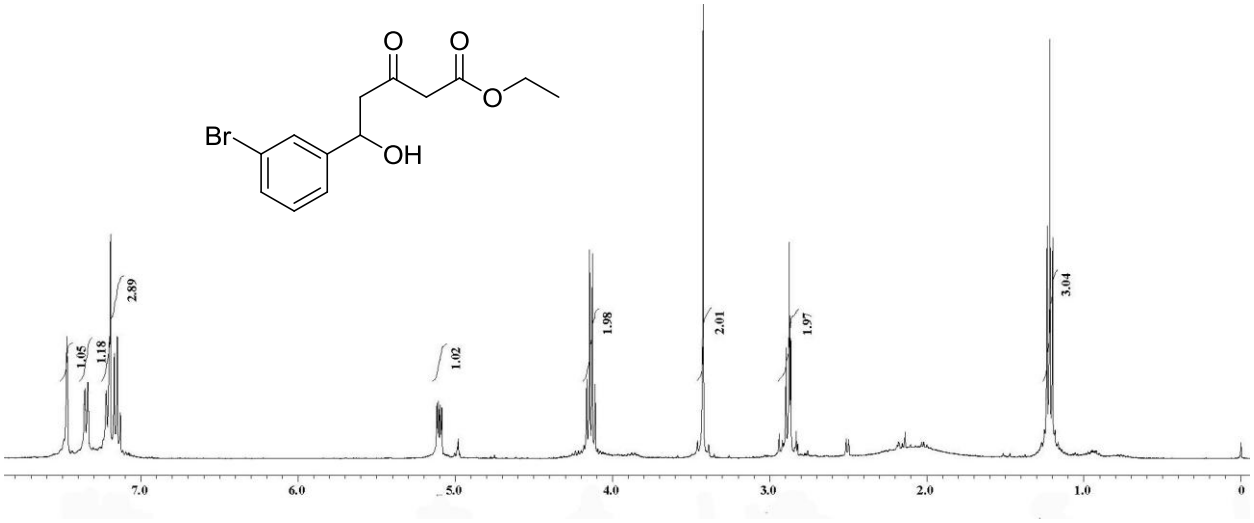

Figure 5: ^{1}H NMR spectrum of **4c** ($CDCl_3$, 400 MHz)

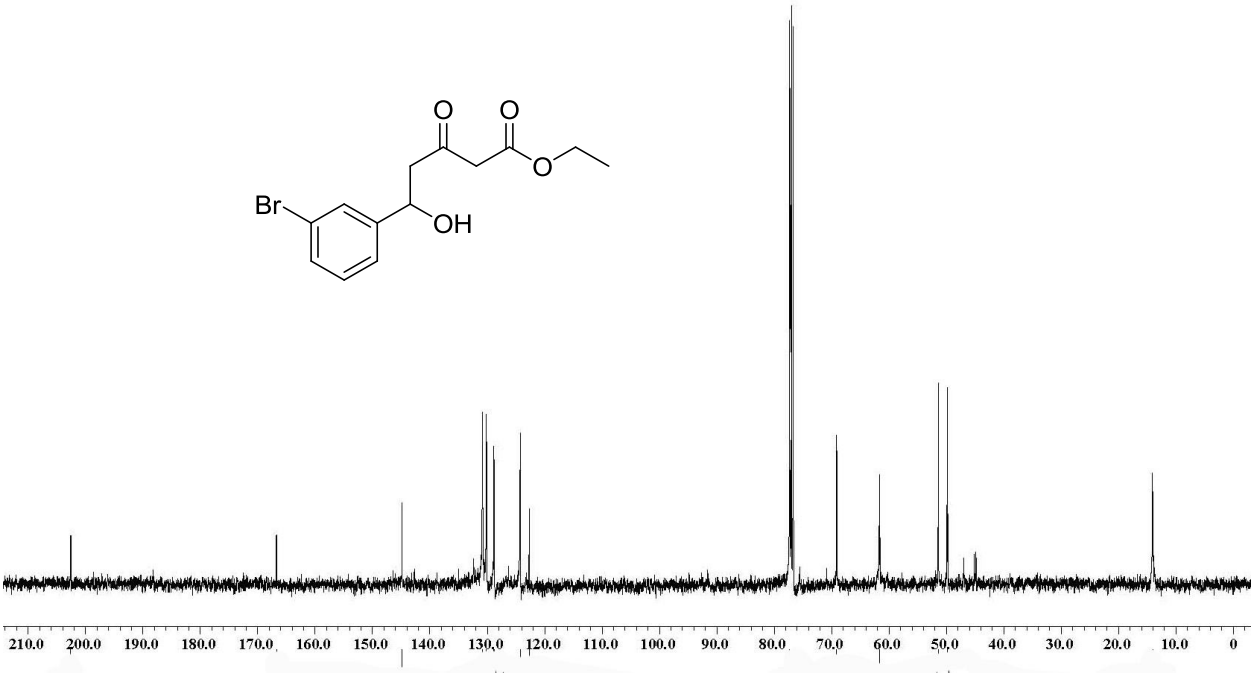

Figure 6: ^{13}C NMR spectrum of **4c** ($CDCl_3$, 100 MHz)

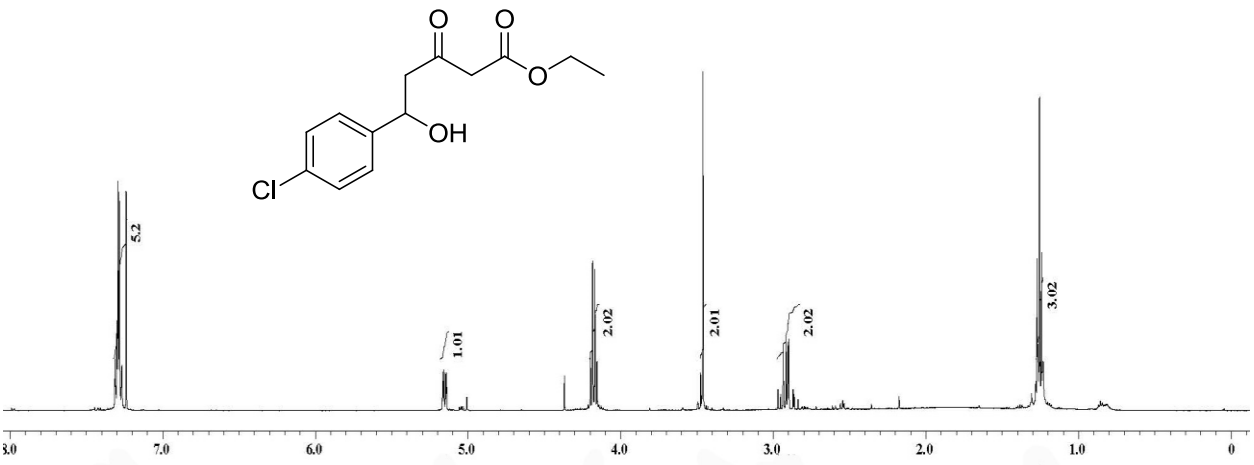

Figure 7: ^{1}H NMR spectrum of **4d** ($CDCl_3$, 500 MHz)

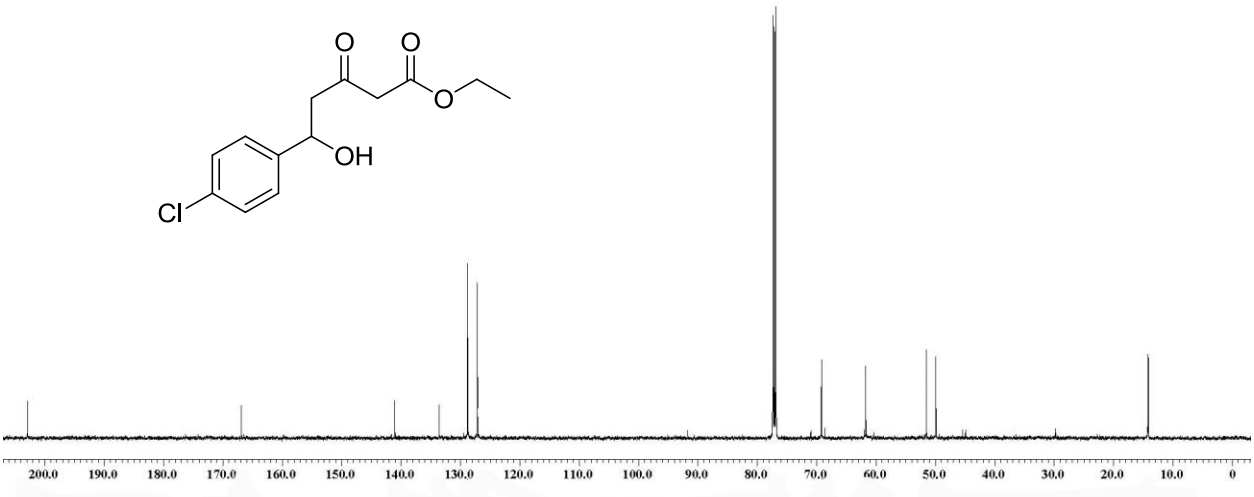

Figure 8: ^{13}C NMR spectrum of **4d** ($CDCl_3$, 125 MHz)

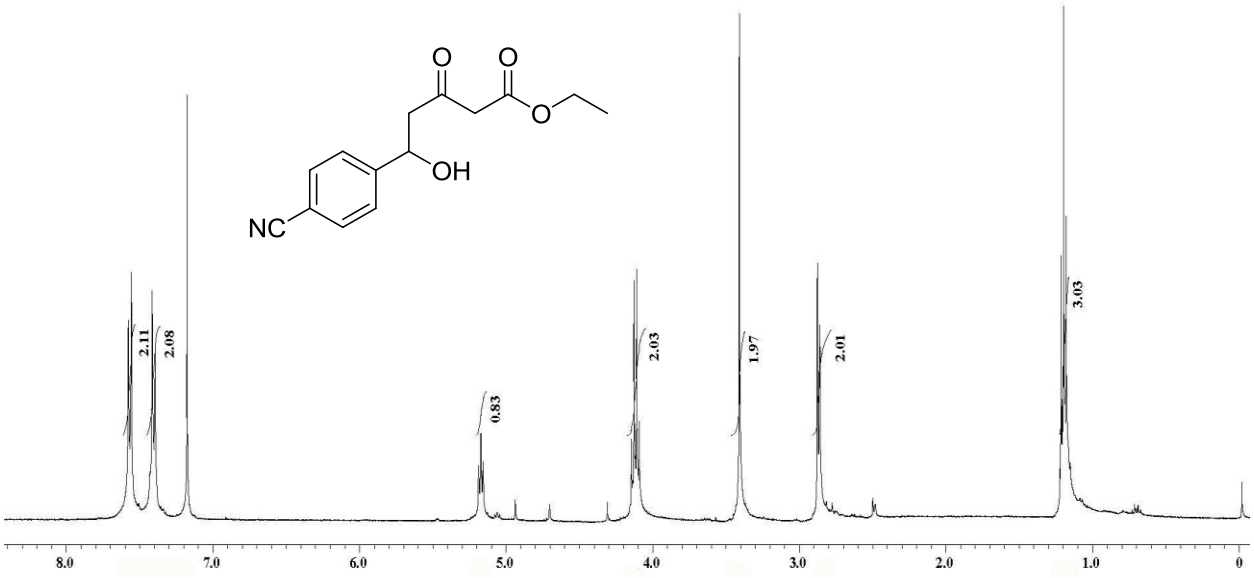

Figure 9: ^{1}H NMR spectrum of **4e** ($CDCl_3$, 400 MHz)

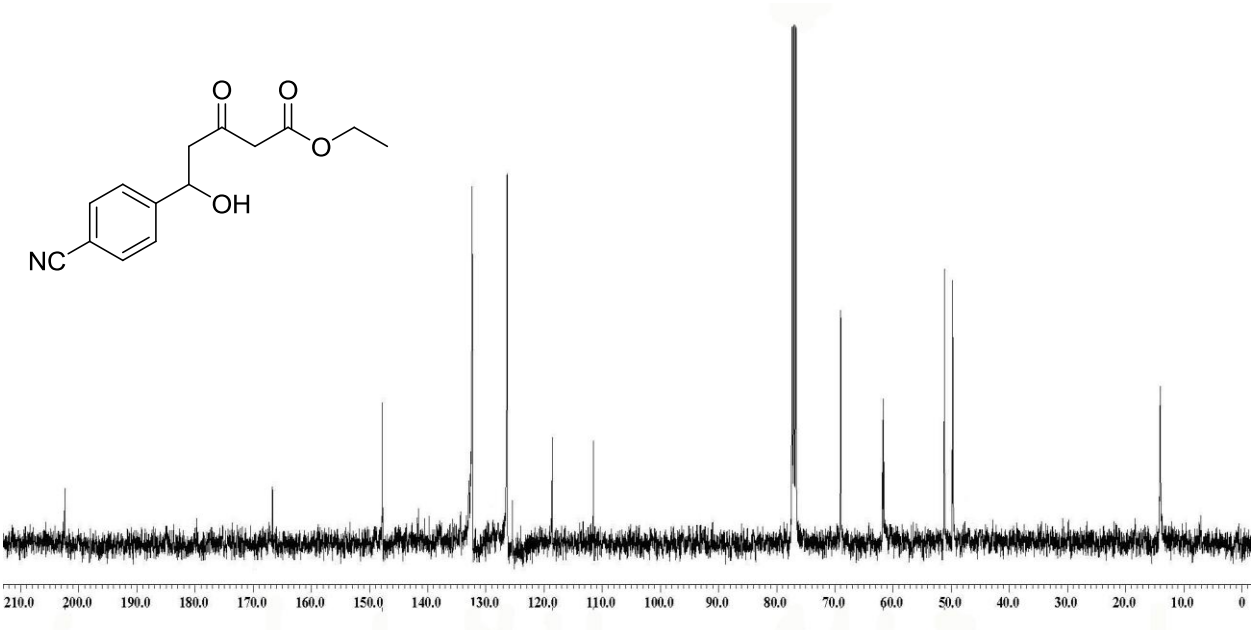

Figure 10: ^{13}C NMR spectrum of **4e** ($CDCl_3$, 100 MHz)

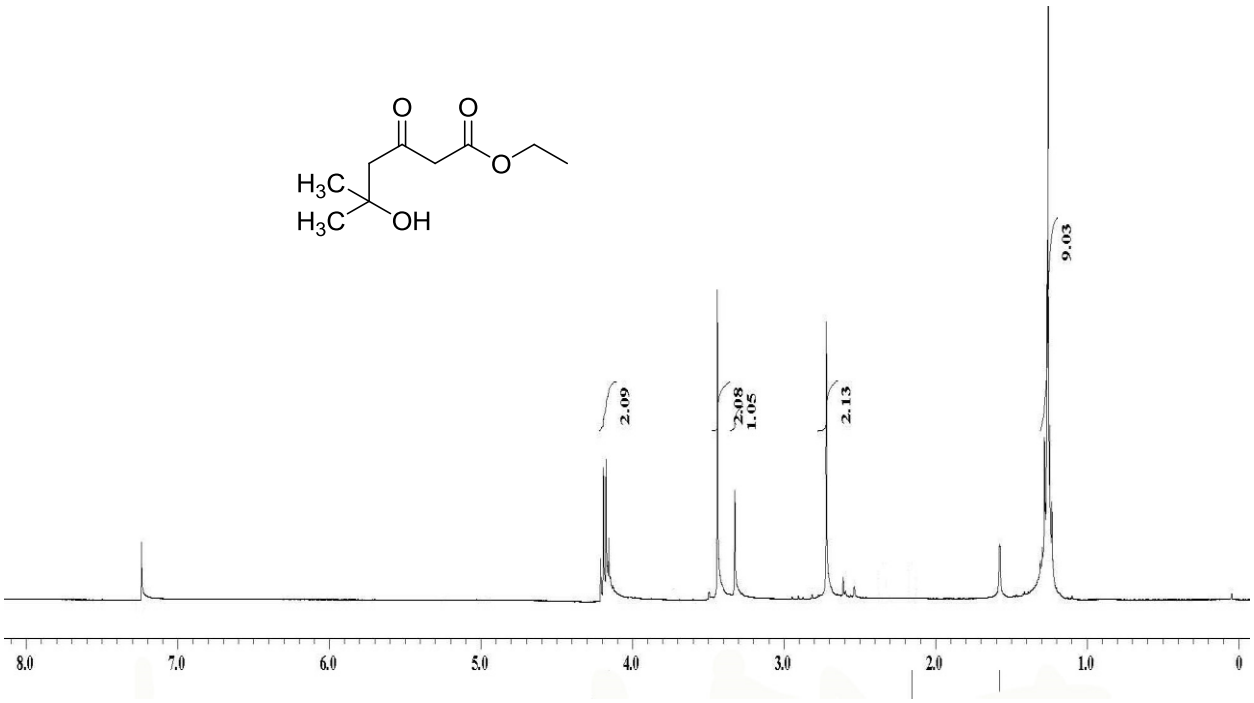

Figure 11: ^{1}H NMR spectrum of **4f** ($CDCl_3$, 400 MHz)

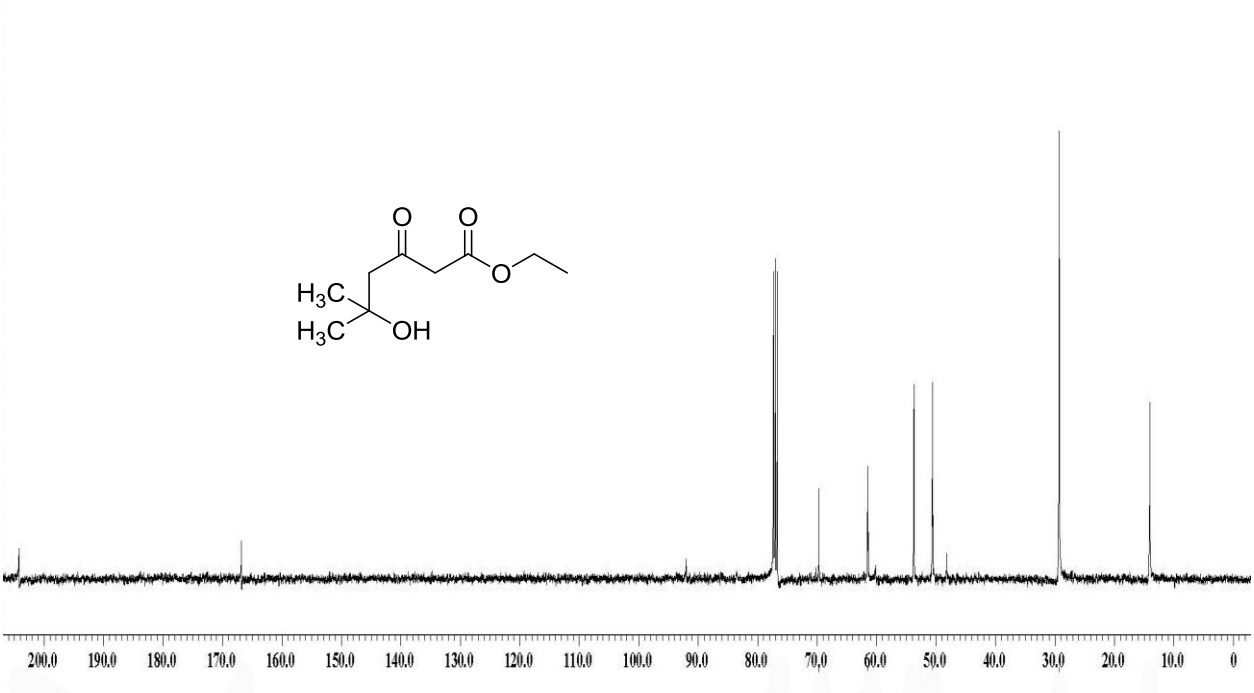

Figure 12: ^{13}C NMR spectrum of **4f** ($CDCl_3$, 100 MHz)

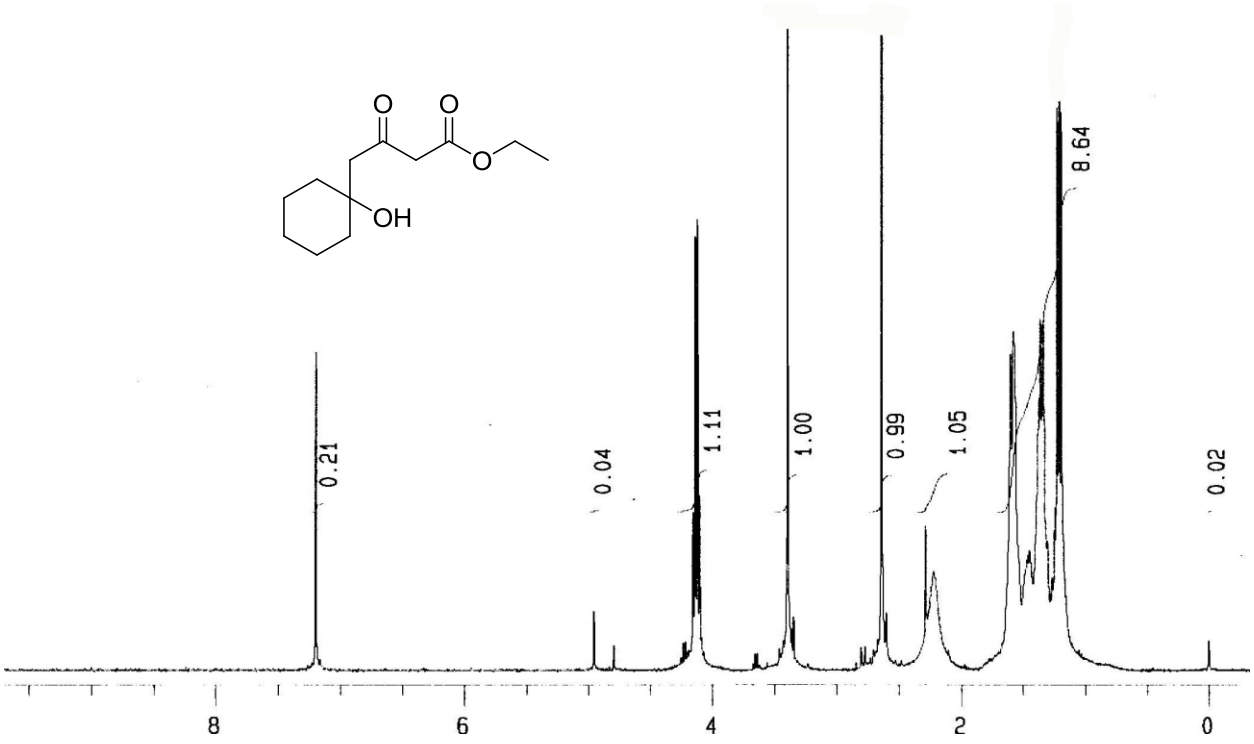

Figure 13: ^{1}H NMR spectrum of **4i** ($CDCl_3$, 400 MHz)

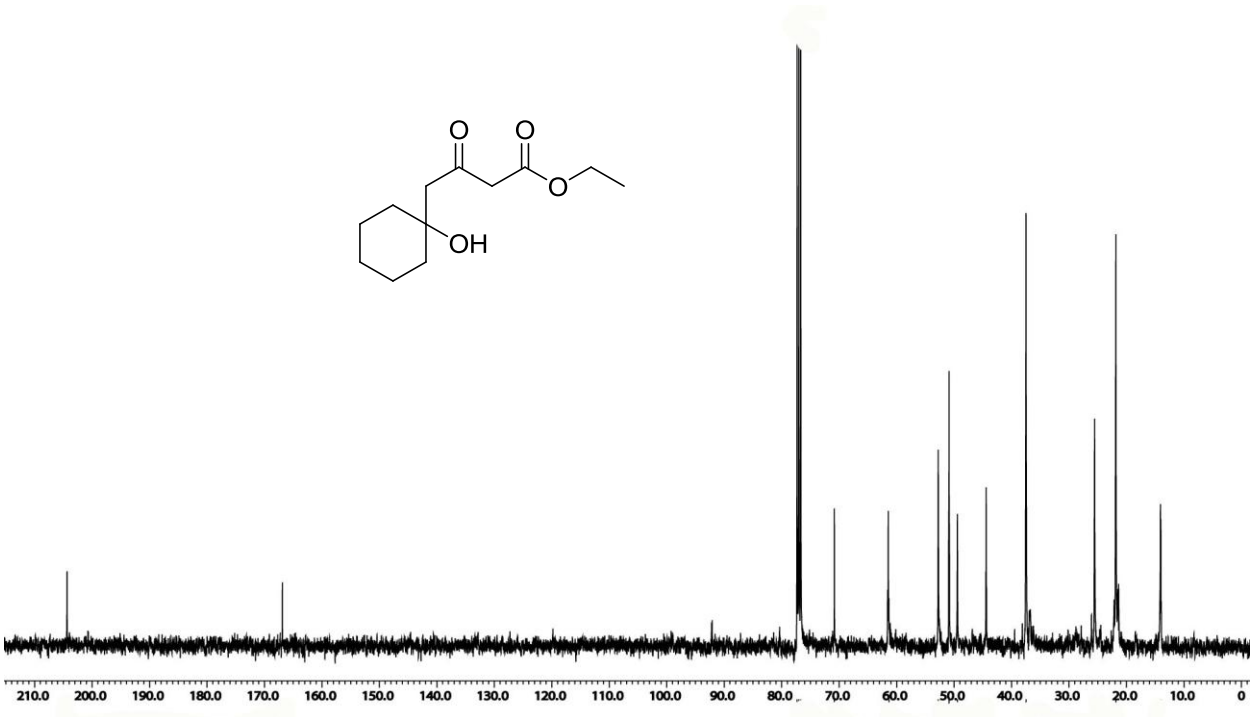

Figure 14: ^{13}C NMR spectrum of **4i** ($CDCl_3$, 100 MHz)

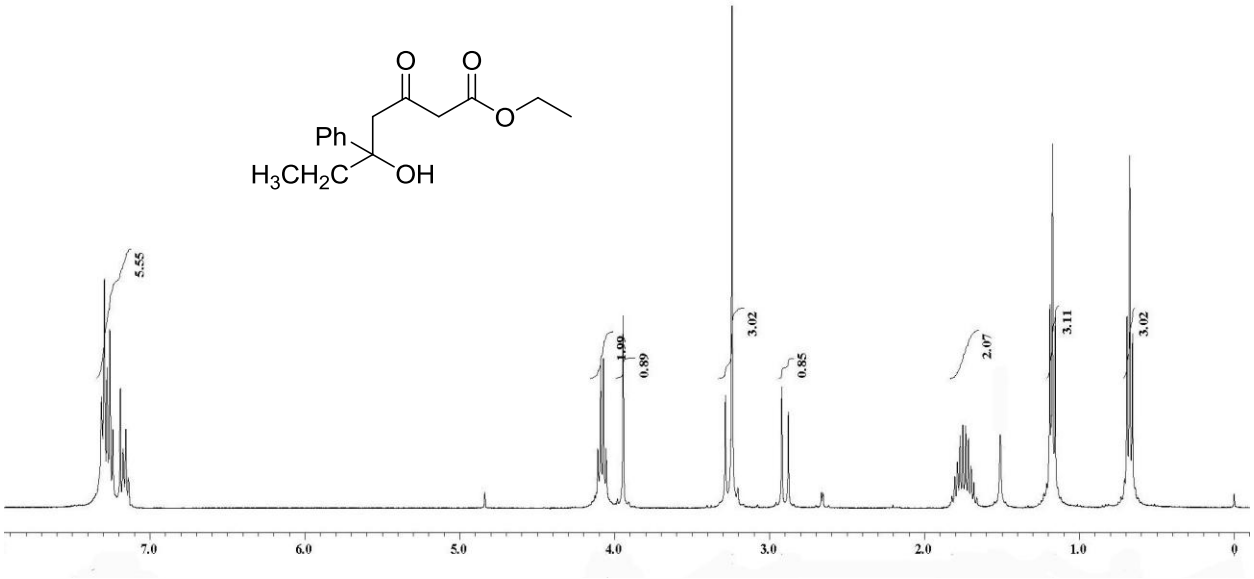

Figure 15: ^{1}H NMR spectrum of **4j** ($CDCl_3$, 400 MHz)

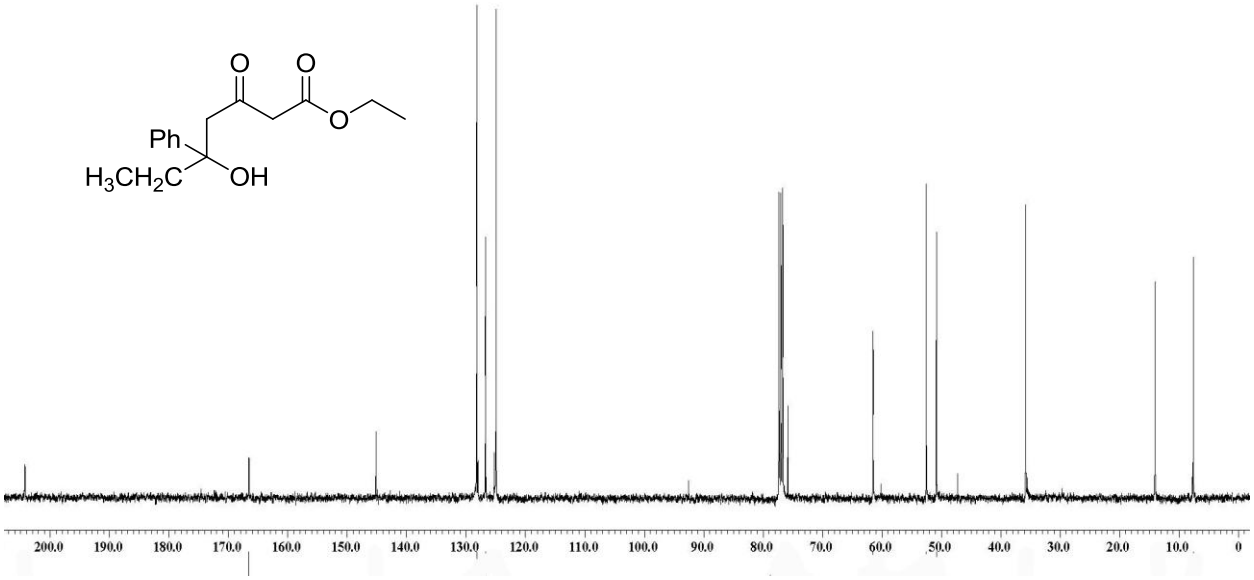

Figure 16: ^{13}C NMR spectrum of **4j** ($CDCl_3$, 100 MHz)

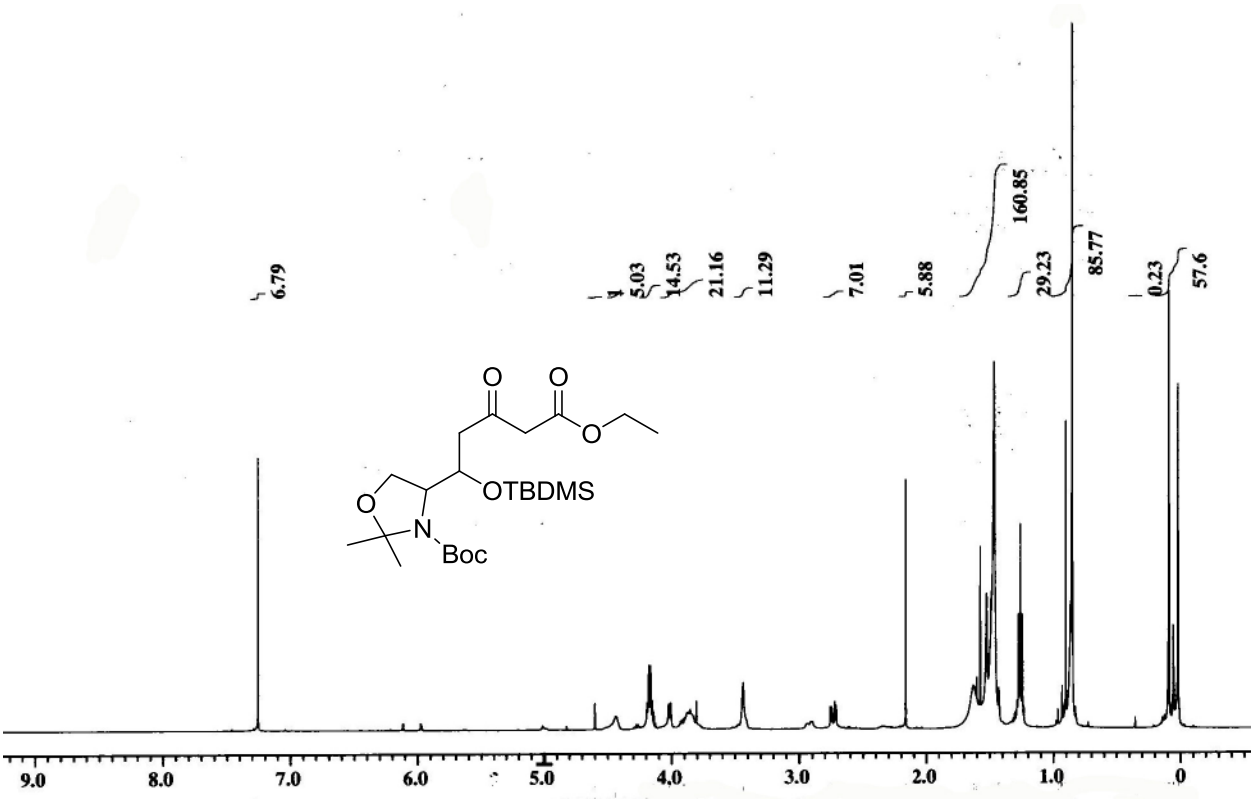

Figure 17: ^{1}H NMR spectrum of **4k** ($CDCl_3$, 500 MHz)

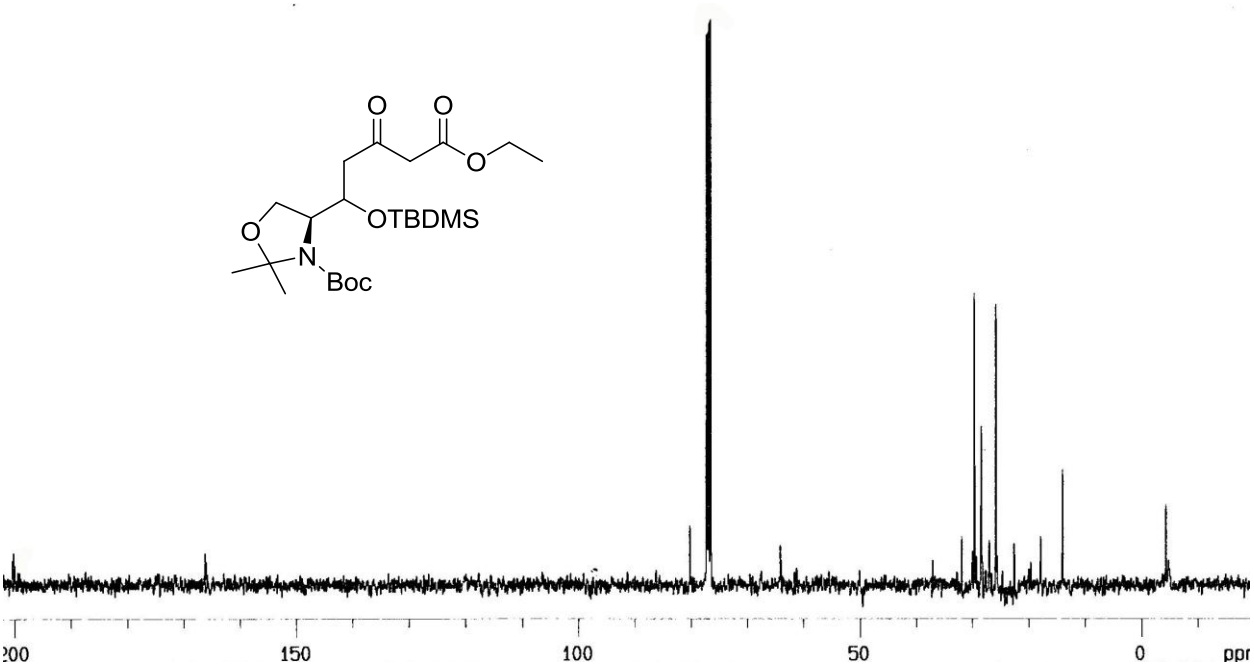

Figure 18: ^{13}C NMR spectrum of **4k** ($CDCl_3$, 125 MHz)

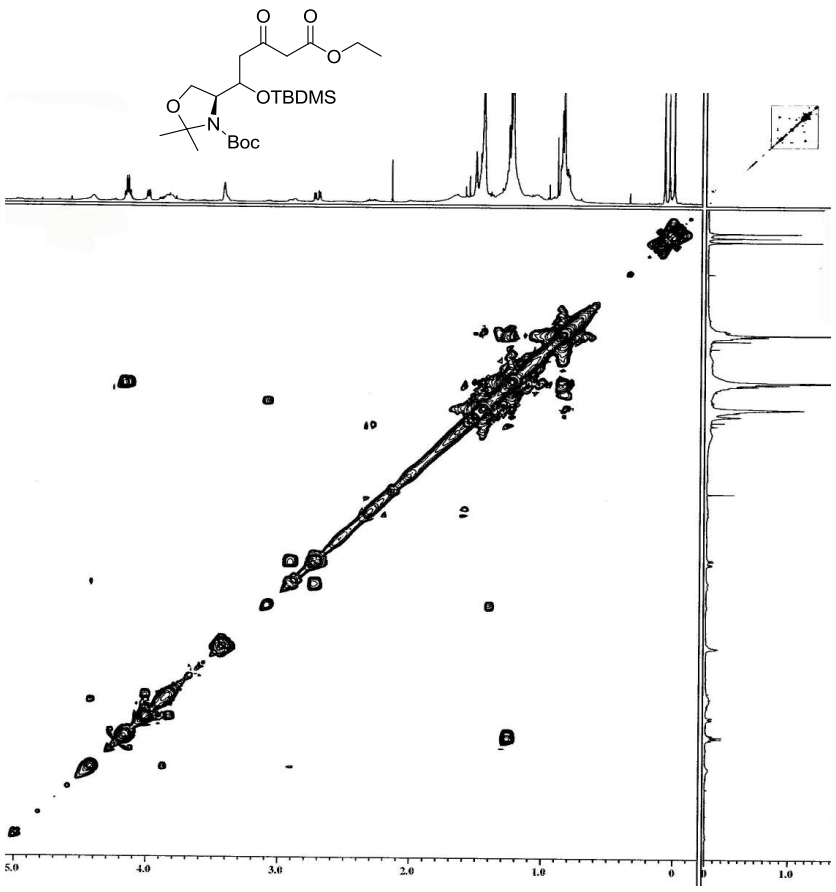

Figure 19: ^{1}H-^{1}H COSY spectrum of **4k** ($CDCl_3$, 500 MHz)

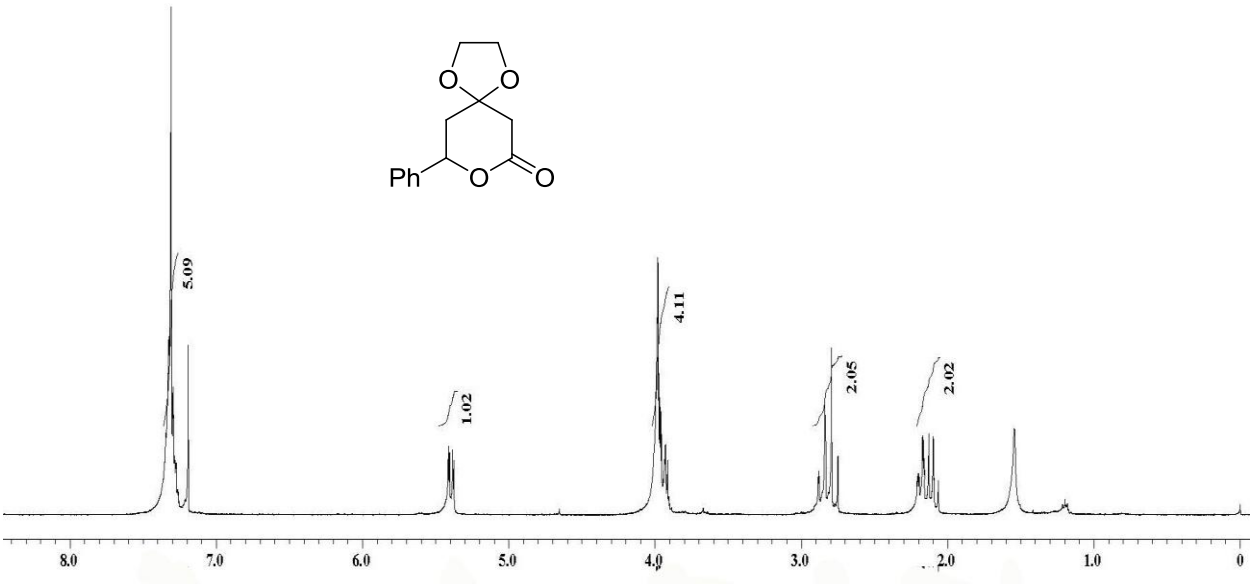

Figure 20: ^{1}H NMR spectrum of **5a** ($CDCl_3$, 400 MHz)

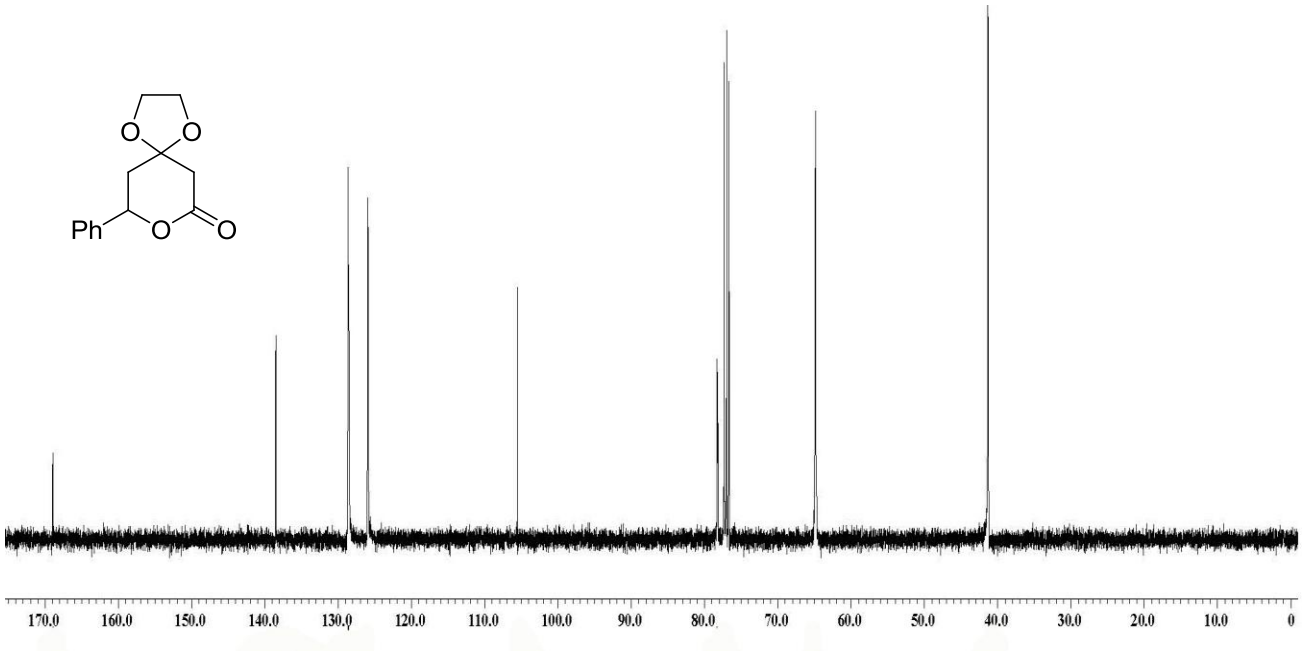

Figure 21: ^{13}C NMR spectrum of **5a** ($CDCl_3$, 100 MHz)

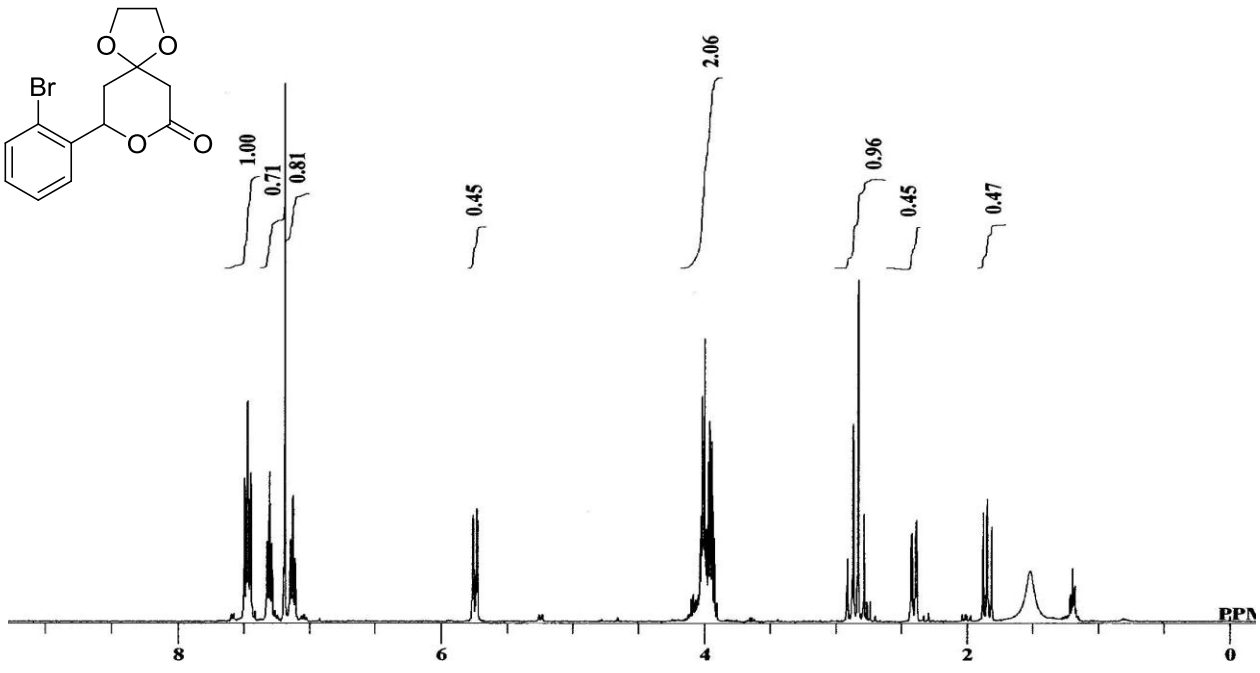

Figure 22: ^{1}H NMR spectrum of **5b** ($CDCl_3$, 400 MHz)

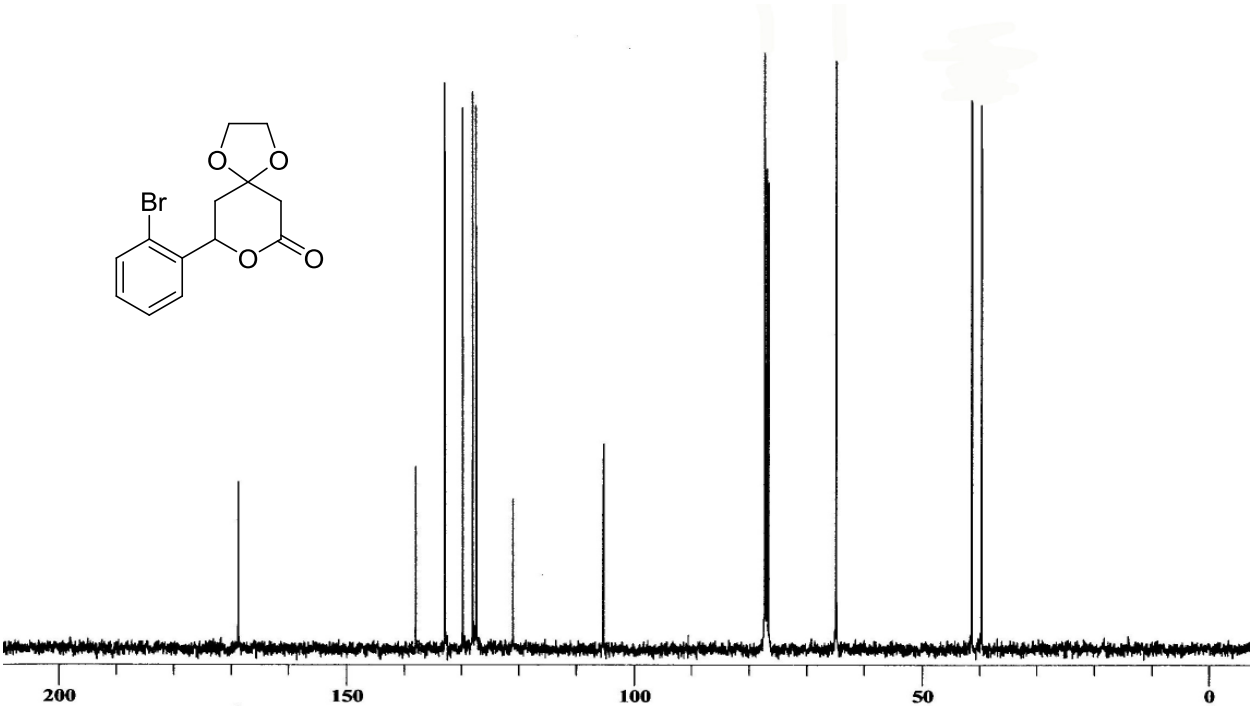

Figure 23: ^{13}C NMR spectrum of **5b** ($CDCl_3$, 100 MHz)

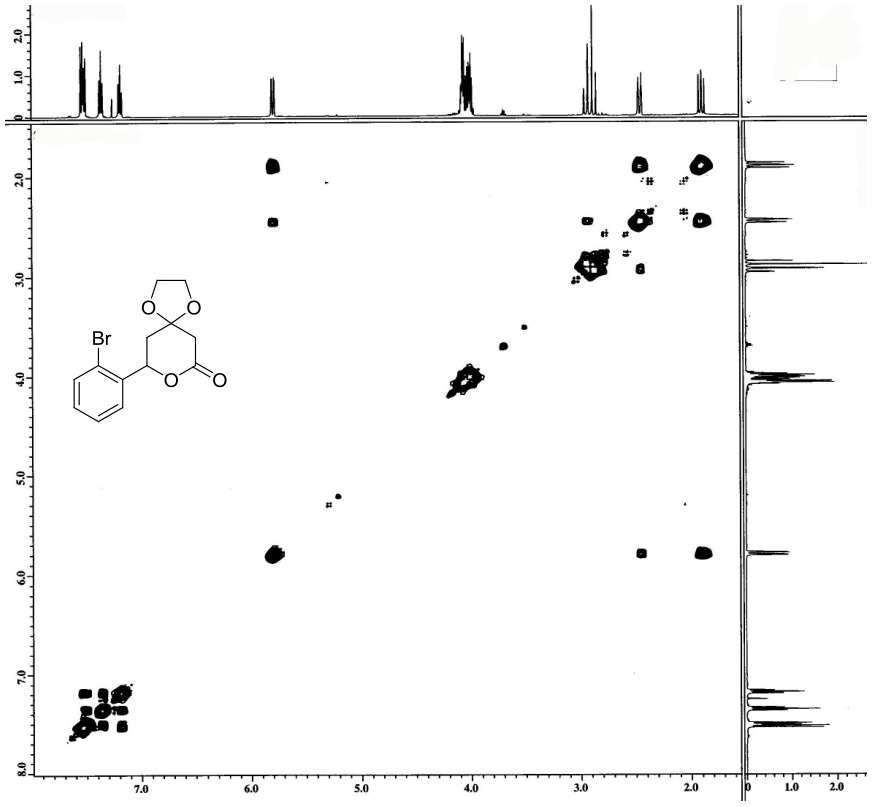

Figure 24: ^{1}H-^{1}H COSY spectrum of **5b** ($CDCl_3$, 500 MHz)

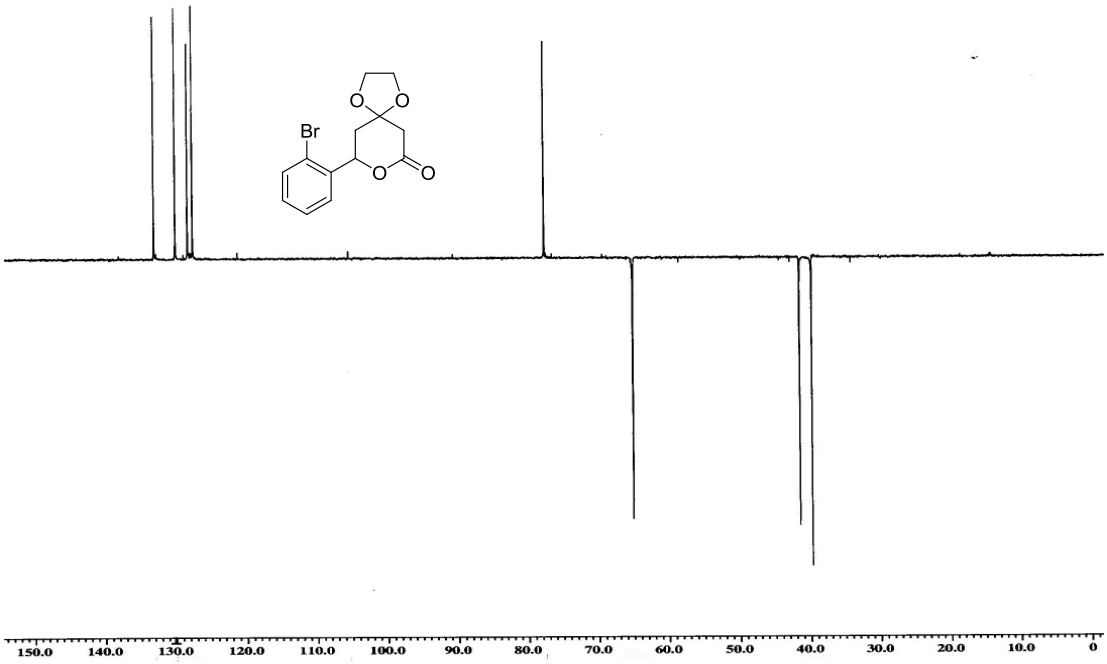

Figure 25: DEPT-135 spectrum of **5b** ($CDCl_3$, 125 MHz)

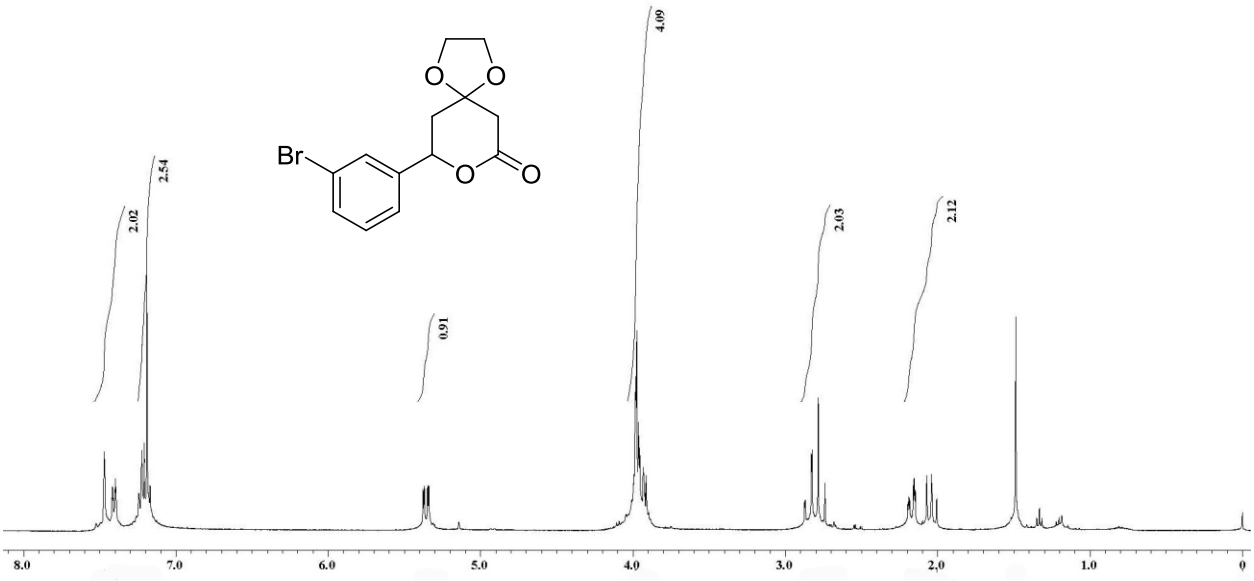

Figure 26: ^1H NMR spectrum of **5c** ($CDCl_3$, 400 MHz)

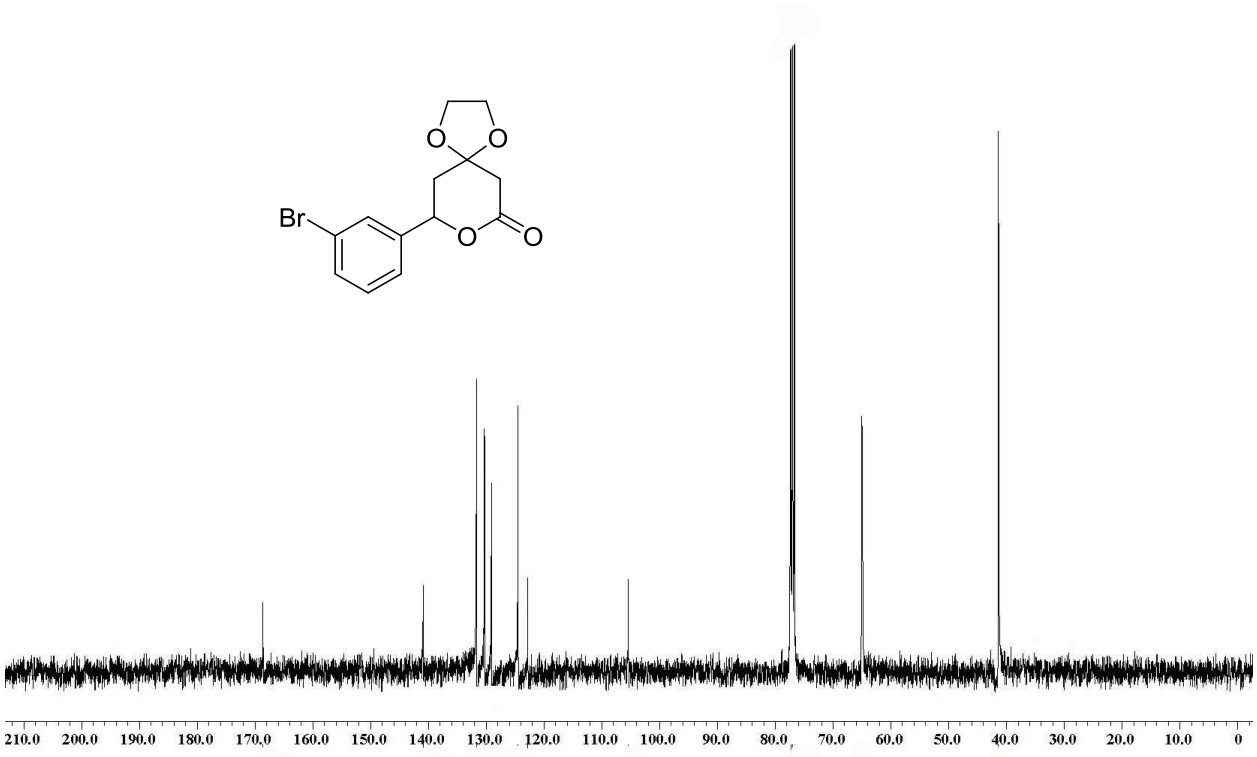

Figure 27: ^{13}C NMR spectrum of **5c** ($CDCl_3$, 100 MHz)

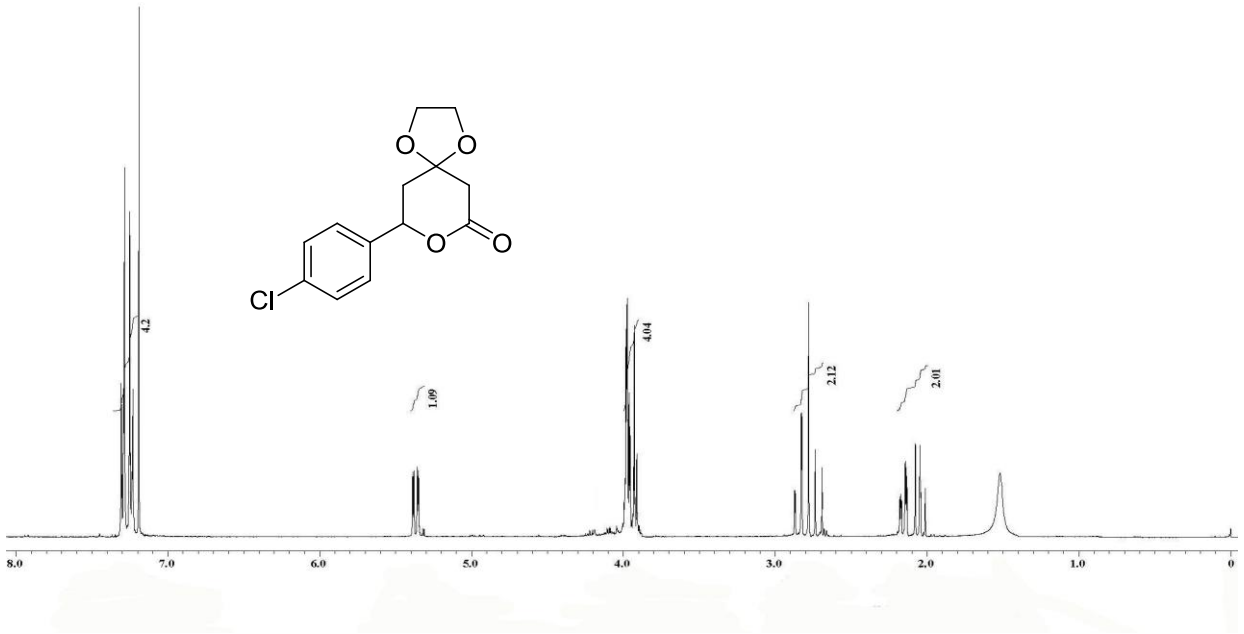

Figure 28: ^{1}H NMR spectrum of **5d** ($CDCl_3$, 500 MHz)

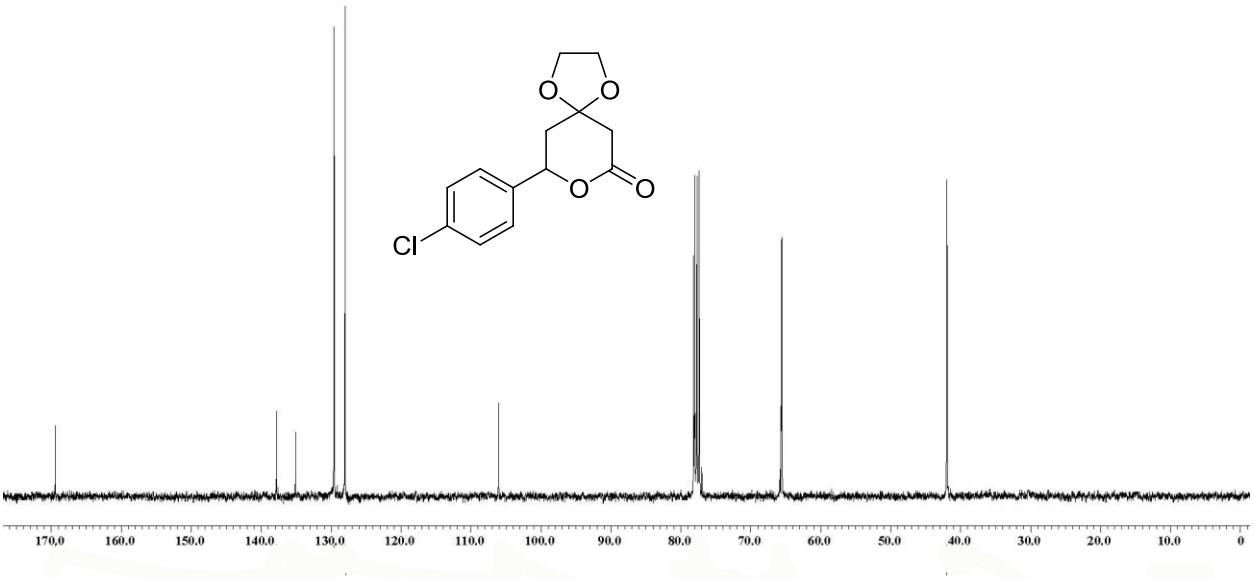

Figure 29: ^{13}C NMR spectrum of **5d** ($CDCl_3$, 125 MHz)

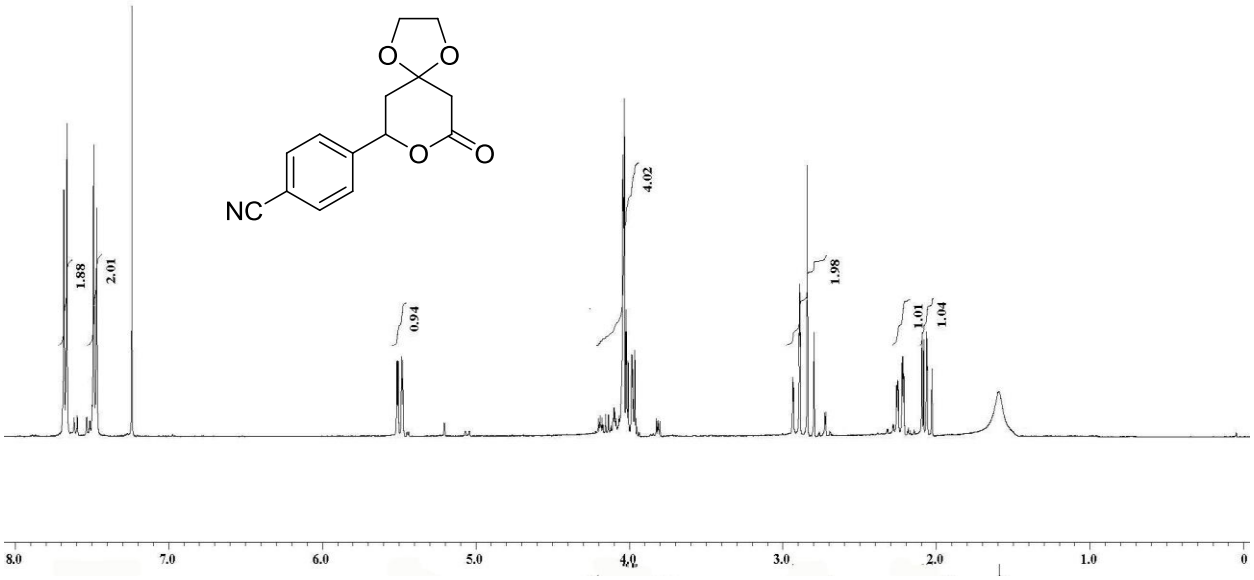

Figure 30: ^{1}H NMR spectrum of **5e** ($CDCl_3$, 500 MHz)

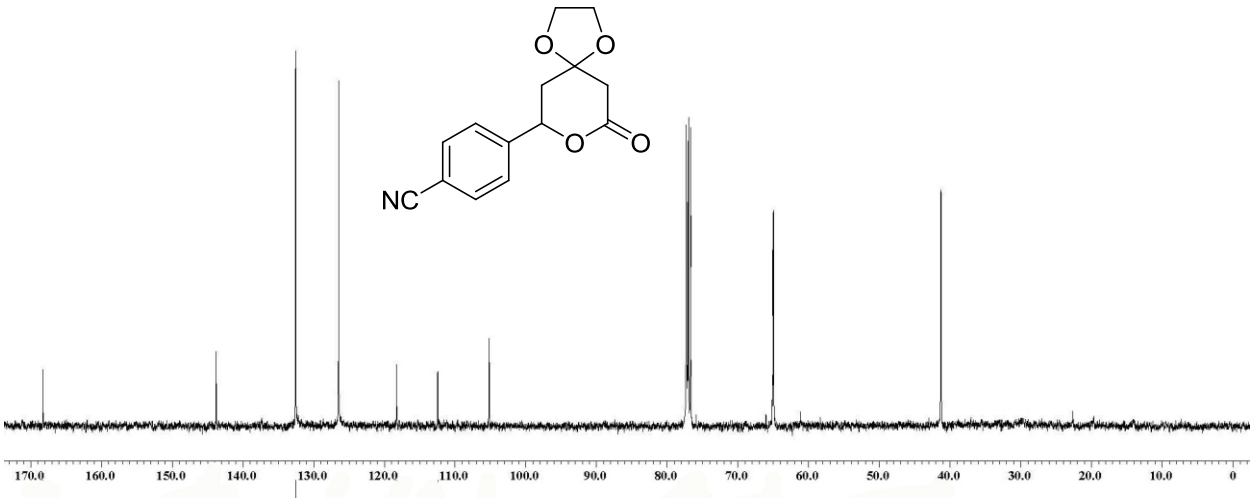

Figure 31: ^{13}C NMR spectrum of **5e** ($CDCl_3$, 125 MHz)

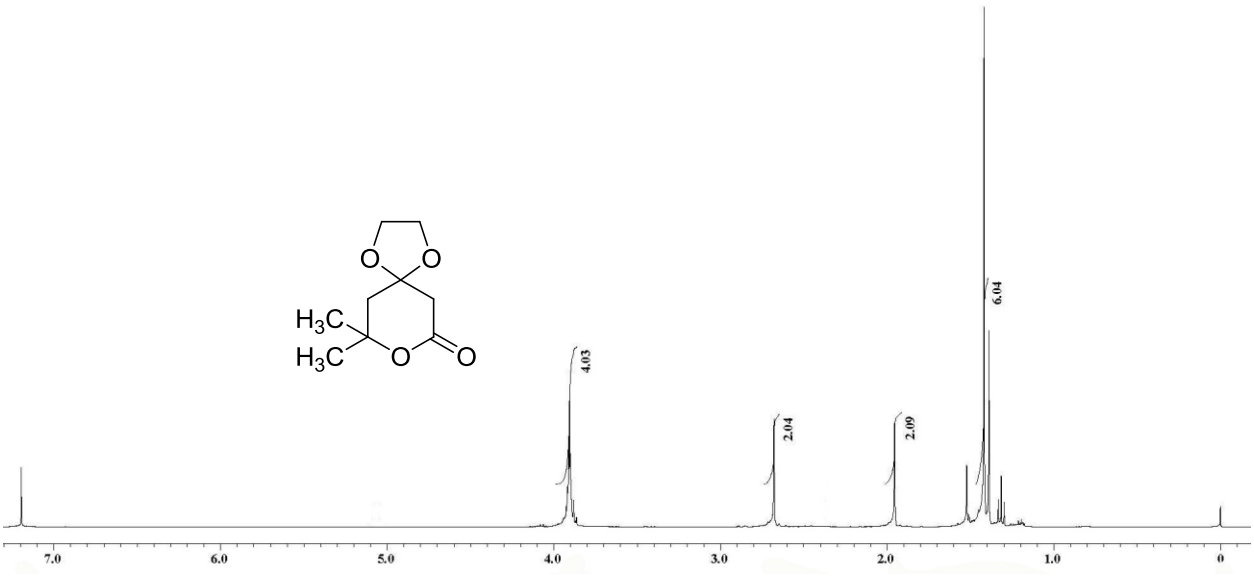

Figure 32: ^{1}H NMR spectrum of **5f** ($CDCl_3$, 400 MHz)

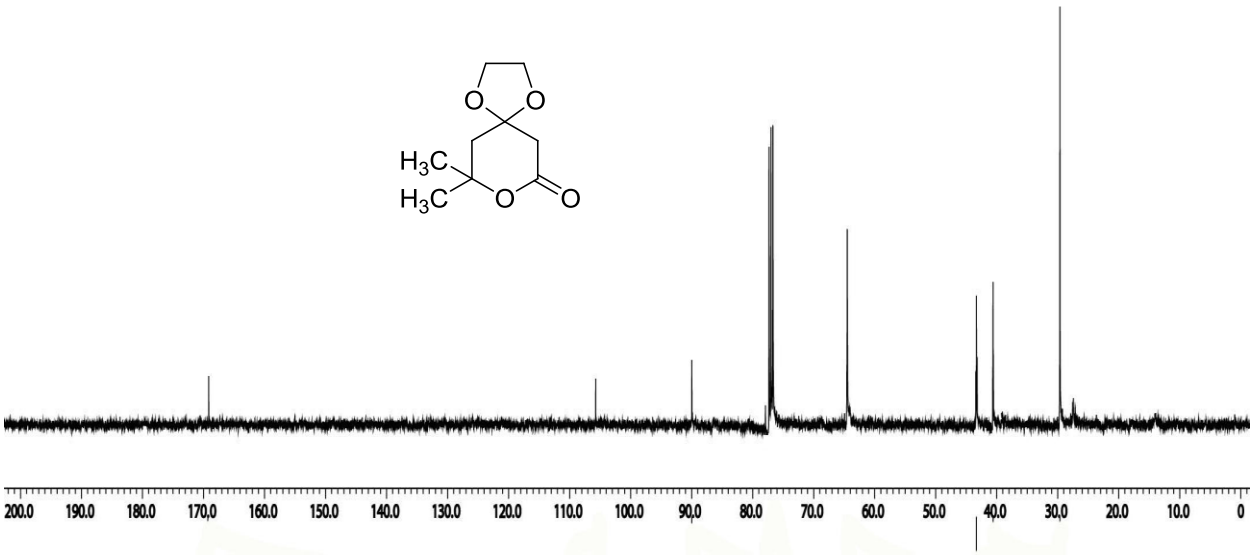

Figure 33: ^{13}C NMR spectrum of **5f** ($CDCl_3$, 100 MHz)

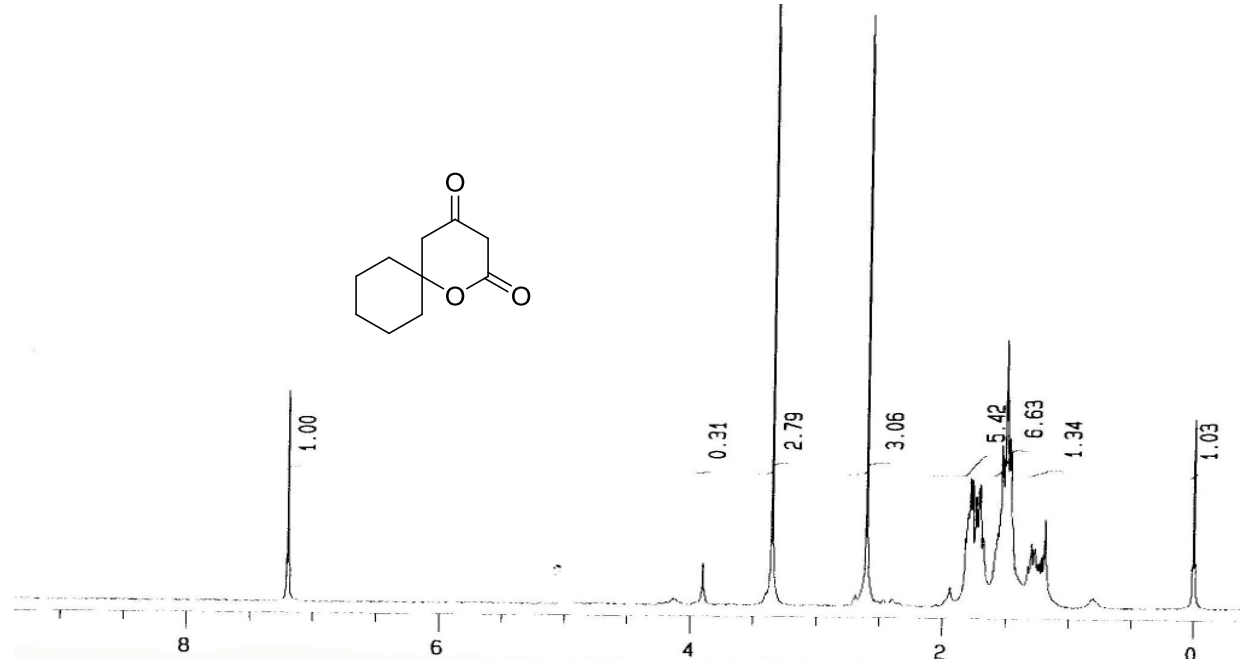

Figure 34: ^{1}H NMR spectrum of **5i** ($CDCl_3$, 400 MHz)

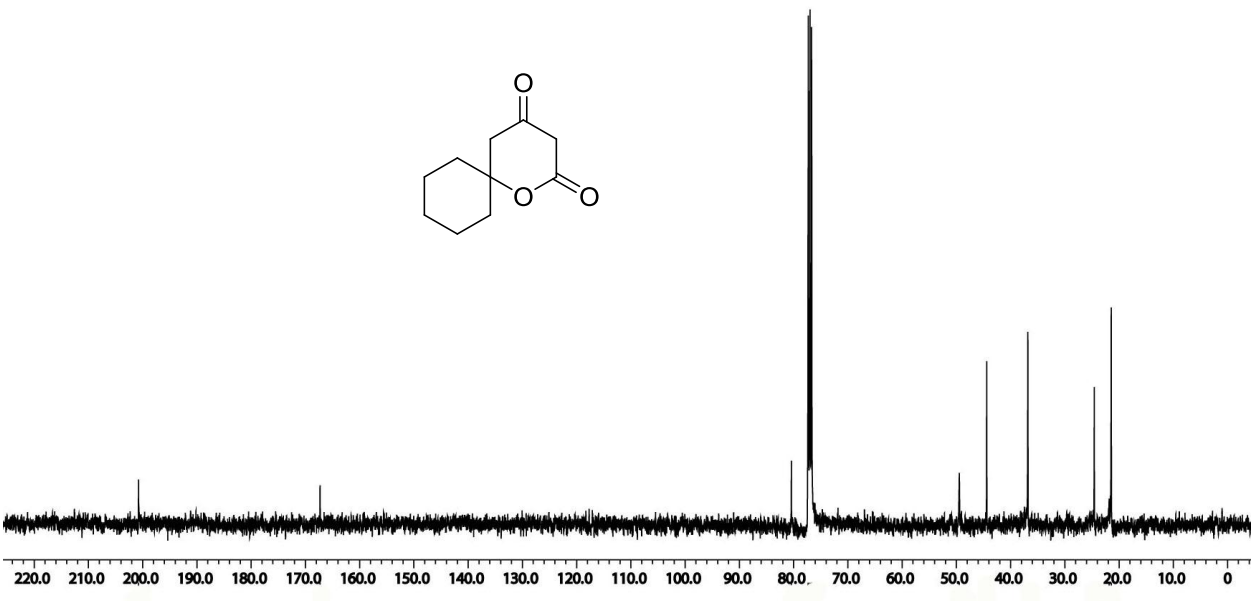

Figure 35: ^{13}C NMR spectrum of **5i** ($CDCl_3$, 100 MHz)

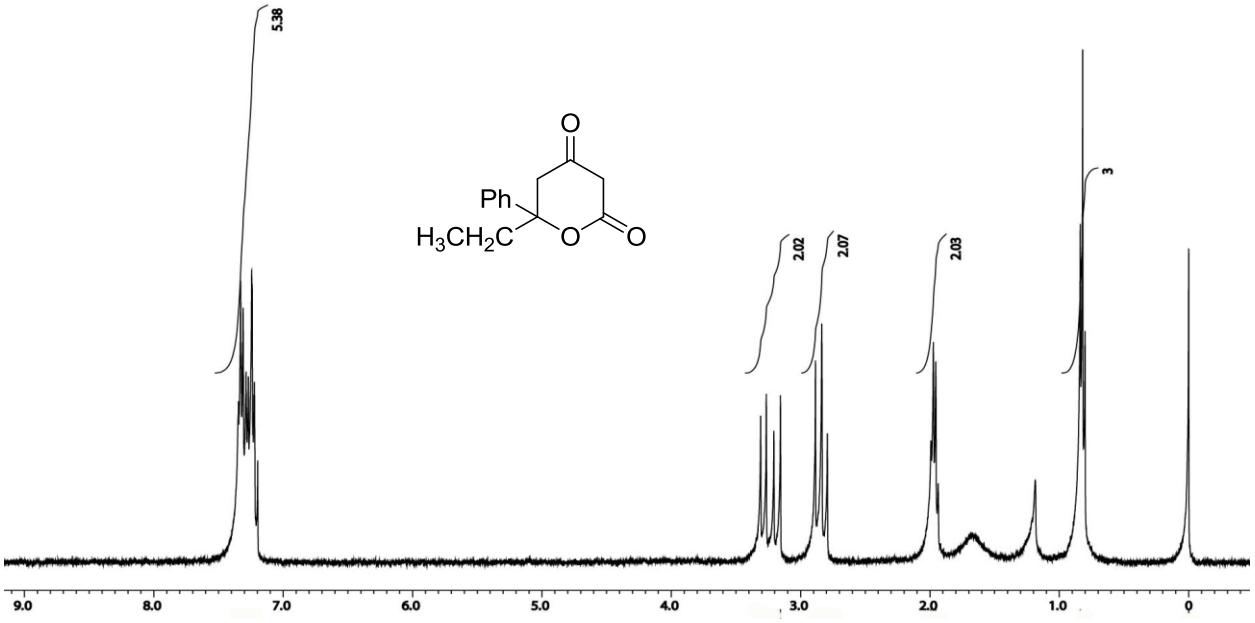

Figure 36: ^{1}H NMR spectrum of **5j** ($CDCl_3$, 400 MHz)

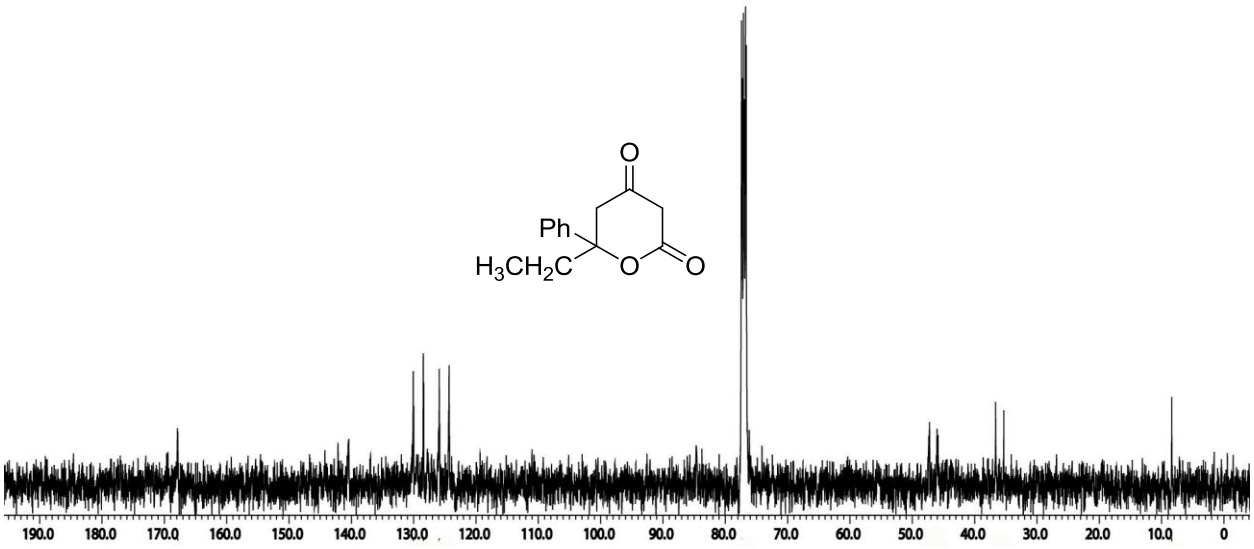

Figure 37: ^{13}C NMR spectrum of **5j** ($CDCl_3$, 100 MHz)

3. X-ray crystallographic studies:

The crystals used in the analyses were glued to a glass fiber and mounted on SMART APEX diffractometer. The instrument was equipped with CCD area detector and data were collected using graphite-monochromated Mo Kα radiation (λ= 0.71069 Å) at low temperature (100K). Cell constants were obtained from the least-squares refinement of three-dimensional centroids through the use of CCD recording of narrow ω rotation frames, completing almost all-reciprocal space in the stated θ range. All data were collected with SMART 5.628 and were integrated with the SAINT[2] program. An empirical absorption correction was applied to collect reflections with SADABS[3] using XPREP[4]. The structure was solved using SIR-97[5] and refined using SHELXL-97[6]. The space group of the compounds was determined based on the lack of systematic absence and intensity statistics. Full matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All the hydrogen atoms are fixed by using geometrical constrains using idealized geometries and have been defined isotropically.

4. X-ray crystal structures :

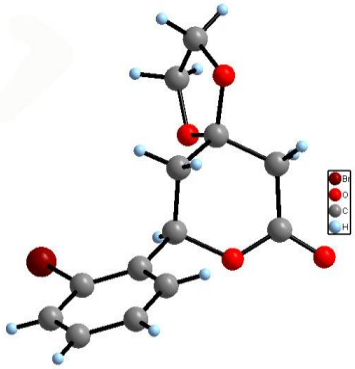

Figure 38: X-ray structure of **5b**

CCDC No. 864222

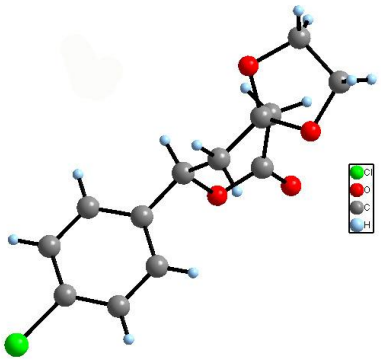

Figure 39: X-ray structure of **5d**

CCDC No. 864223

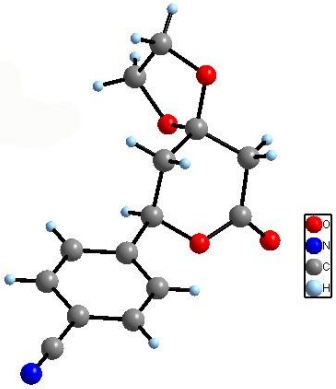

Figure 40: X-ray structure of **5e**

CCDC No. 864224

5. X-ray crystallographic data and structure refinement (Table 1):

Compounds	**5b**	**5d**	**5e**
Formula	$C_{13}H_{13}BrO_4$	$C_{13}H_{13}ClO_4$	$C_{14}H_{13}NO_4$
Formula Weight	313.1439	268.6929	259.2573
Crystal System	Triclinic	Monoclinic	Monoclinic
Space Group	P-1	C2/c	P21/c
T, **K**	100 (2)	100 (2)	100 (2)
Z	2	4	4
a, **Å**	7.715 (5)	24.847 (5)	15.209 (5)
b, **Å**	8.522 (6)	5.362 (6)	8.498 (5)
c, **Å**	9.869 (4)	19.109 (3)	10.002 (5)
α, **deg**	79.064(5)	90.000(5)	90.000(5)
β, **deg**	86.523 (6)	112.004(5)	107.986 (5)
γ, **deg**	72.387(4)	90.000(5)	90.000(5)
V, **Å^3**	607.2 (6)	2360 (2)	1229.5 (10)
d_{calcd}, g/cm^3	1.713	1.512	1.401
μ, **mm^{-1}**	3.388	0.327	0.104
θ range, **deg**	0.60-0.65	3.39-26.49	2.82-26.50
GOF (F^2)	1.056	1.157	1.075
R_1[b] (wR_2[c]), %	0.0563 (0.1203)	0.0612 (0.1364)	0.0617 (0.1241)

[a] [a] Mo Kα radiation, [b]$R_1 = \sum \| F_0 | - | F_c \| / \sum | F_0 |$, [c]$wR_2 = \{\sum[w(F_0^2 - F_c^2)^2] / \sum[w(F_0^2)^2]\}^{1/2}$

6. References.

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2. SAINT^{+} 6.02ed.; Bruker AXS, Madison, WI, 1999.

3. Sheldrick, G. M. SADABS, Empirical Absorption Correction Program, University of Göttingen, Göttingen, Germany, 1997.

4. XPREP, 5.1ed. Siemens Industrial Automation Inc., Madison, WI, 1995.

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6. Sheldrick, G. M. SHELXL-97: Program for Crystal Structure Refinement (University of Göttingen, Göttingen, Germany, 1997.