Electronic Supplementary Material (ESI) for RSC Advances.
This journal is © The Royal Society of Chemistry 2016

Efficient Epoxide Isomerization within a Self-Assembled Hexameric Organic Capsule

Thomas Caneva,[a] Laura Sperni,[a] Giorgio Strukul,[a] Alessandro Scarso[a,*]

a) Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari di Venezia, via Torino 155, Mestre (VE), 30172 (ITALY). Fax: +39-041-2340517; Tel:+39-041-2348569. E-mail: alesca@unive.it

Reagents and Materials.

General

^{1}H NMR were recorded at 298 K, unless otherwise stated, on a Bruker AVANCE 300 spectrometer operating at 300.15 MHz. δ values in ppm are relative to $SiMe_4$. GC analysis were performed on HP SERIES II 5890 equipped with a HP5 column (30 m, I. D. 0.25 m, film 0.25 μm) using He as gas carrier and FID. GC-MS analyses were performed on a GC Trace GC 2000 equipped with a HP5-MS column (30 m, I.D. 0.25 mm, film 0.25 μm) using He gas carrier and coupled with a quadrupole MS Thermo Finnigan Trace MS with *Full Scan* method.

Solvents and reactants were used as received; otherwise they were purified as reported in the literature.[1] TLC analysis were performed on TLC Polygram ® Sil G/UV254 of 0.25 mm thickness and flash-chromatography separations were performed on silica gel Merk 60, 230-400 mesh.[2]

Substrates and capsule

Styrene oxide, 4-chlorostyrene oxide, *α*-methyl-styrene oxide, 3-nitrostyrene oxide, 3-vinyl-anisole oxide, 3-chlorostyrene oxide, 3-bromostyrene oxide, *trans*-stilbene oxide, cyclopentene oxide, cyclohexene oxide, cyclooctene oxide, *α*-pinene oxide, *exo*-2,3-epoxynorbornane, 1,2-epoxy-octane, *cis*-2,3-epoxybutane, propylene oxide, vinyl-cyclohexene dioxide, *trans*-1,3-difenil-2,3-epoxypropan-1-one, methyl-trans-3-(4-methoxyphenyl)-glycidate, tetrabutylammonium bromide **4**, *n*-hexyl-resorcinol, acetic acid are all commercially available products and were used as received without any further purification. Resorcin[4]arene[3] **1** and *cis*-stilbene oxide **2i**[4] were prepared as reported in the literature. All the carbonyl products were identified by GC-MS and ^{1}H-NMR analysis.

Catalytic Studies

Catalytic isomerization of epoxides mediated by the hexameric capsule

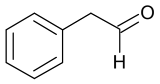
In a 3 mL vial were introduced a water saturated chloroform solution of resorcin[4]arene **1** (36 mM, 1.5 mL) followed by the proper epoxide (14 eq. with respect to resorcin[4]arene capsule) and the resulted mixture was stirred at 750 rpm until completely homogeneous. The vial was sealed and thermostatted at 60°C. The reaction progress was followed by GC or ^{1}HNMR analyses sampling the reaction mixture at different times and diluting the sample with water saturated chloroform. The isomerization products were confirmed by GC-MS and ^{1}H NMR.

Experimental procedure as above reported was repeated adding tetrabutylammonium bromide **4** (8 equivalents with respect to the capsule) together with the substrates in order to carry out control tests of the catalytic activity of the activity within the capsule.

Catalytic epoxide isomerization reaction of styrene oxide with Acetic Acid or with 4-hexyl-resorcinol

The procedure is the same as above replacing the capsule with acetic acid (6 mM) or 4-hexyl-resorcinol (24 equivalents with respect to the capsule, 140 mM).

phenylacetaldehyde 3a



^{1}H NMR spectrum was in agreement with characterization already reported in the literature.[5]

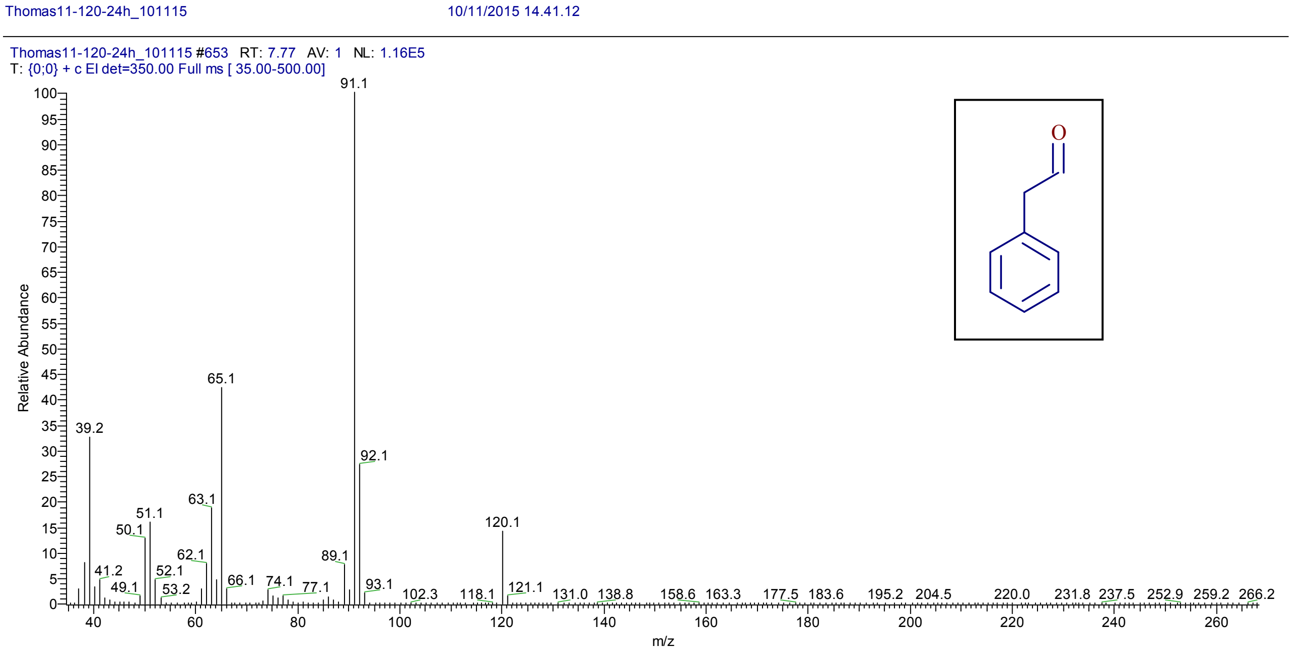
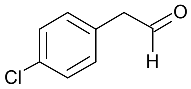


Figure 1. Mass spectrum of phenylacetaldehyde **3a**.

(4-chlorophenyl)acetaldehyde 3b



^{1}H NMR spectrum was in agreement with characterization already reported in the literature.[6]

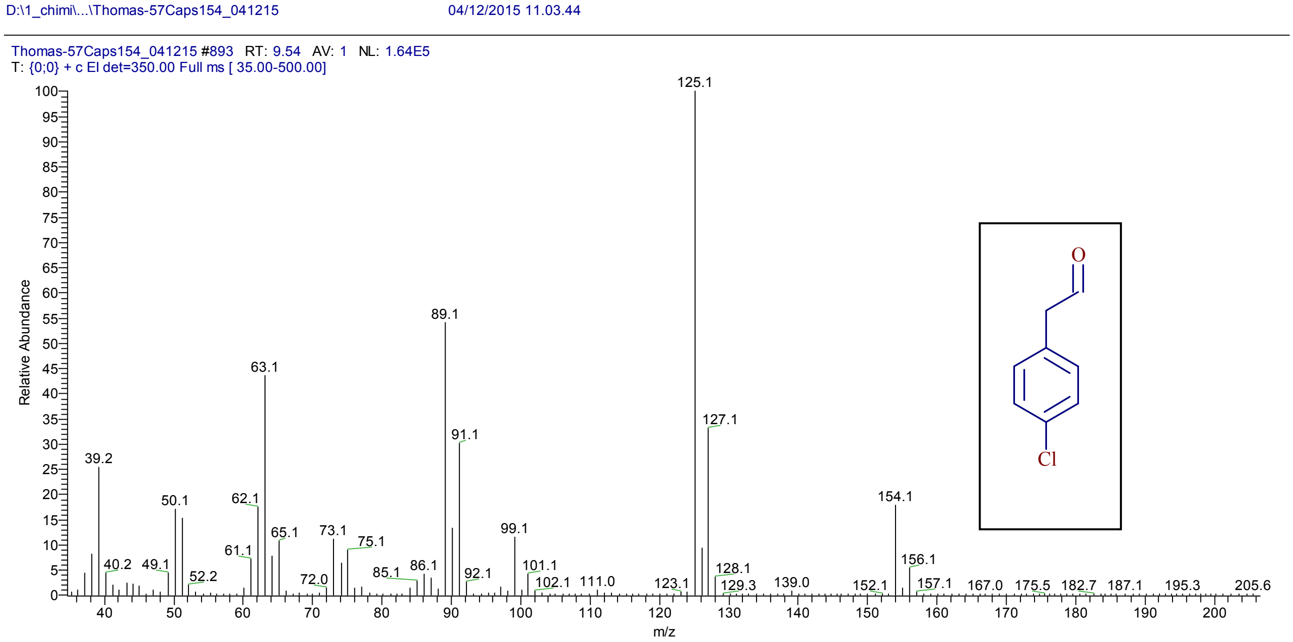
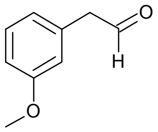


Figure 2. Mass spectrum of (4-chlorophenyl)acetaldehyde **3b**.

(3-methoxyphenyl)acetaldehyde 3c



^{1}H NMR spectrum was in agreement with characterization already reported in the literature.[7]

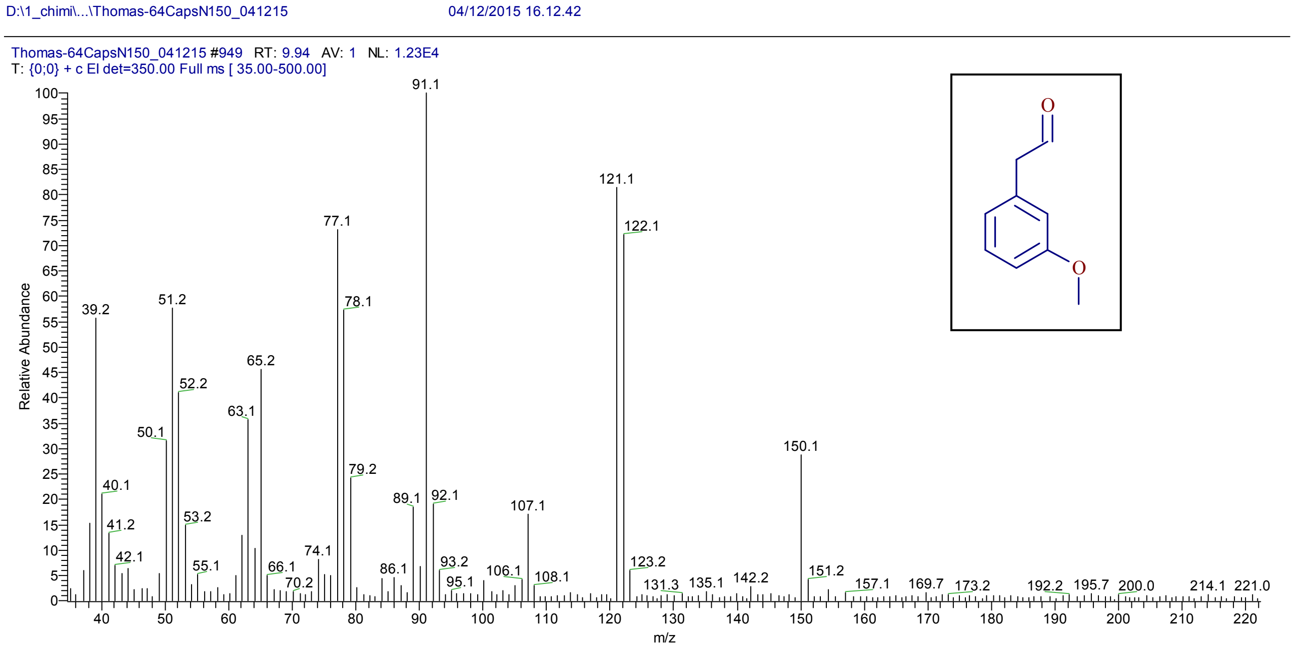
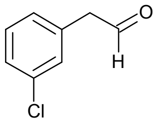


Figure 3. Mass spectrum of (3-methoxyphenyl)acetaldehyde **3c**.

(3-chlorophenyl)acetaldehyde 3d.



^{1}H NMR spectrum was in agreement with characterization already reported in the literature.[8]

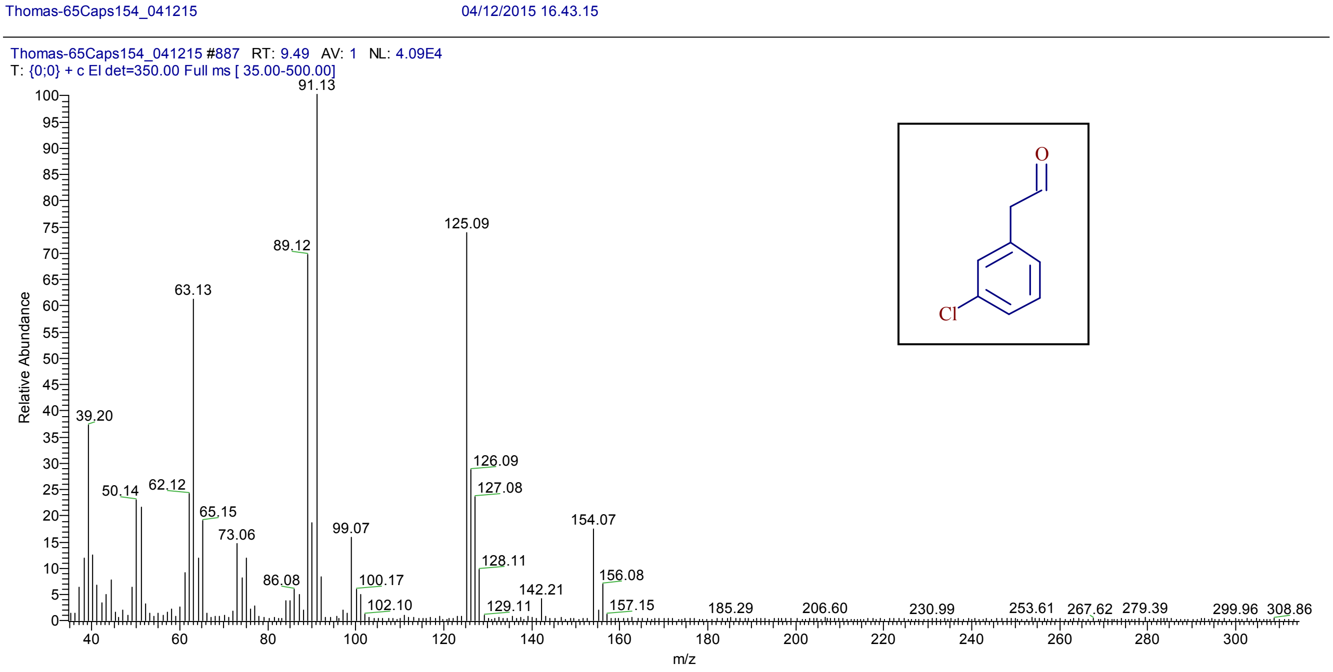
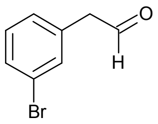


Figure 4. Mass spectrum of (3-chlorophenyl)acetaldehyde **3d**.

(3-bromophenyl)acetaldehyde 3e



^{1}H NMR spectrum was in agreement with characterization already reported in the literature.[8]

D:\1_chimi\...\Thomas3-198conc2_090616 09/06/2016 14.43.32

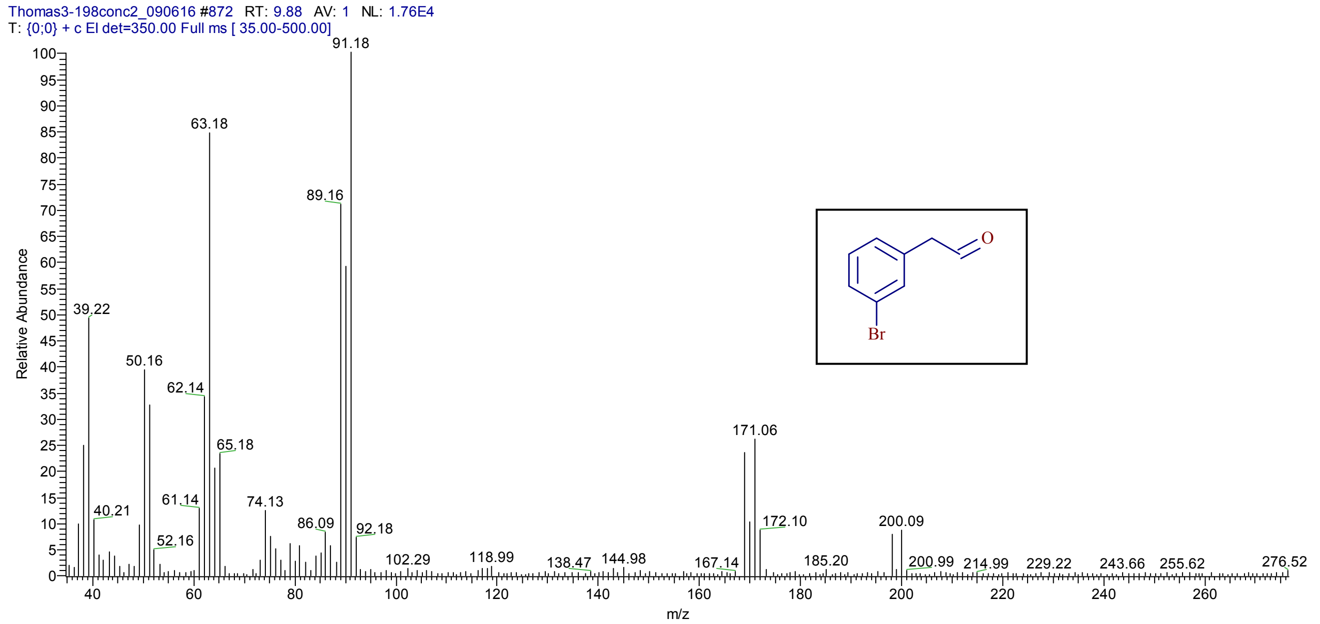
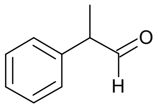


Figure 5. Mass spectrum of (3-bromophenyl)acetaldehyde **3e**.

2-phenylpropanal 3g



^{1}H NMR spectrum was in agreement with characterization already reported in the literature.[9]

D:\1_chimi\...\Thomas-59Caps134_041215 04/12/2015 14.40.22

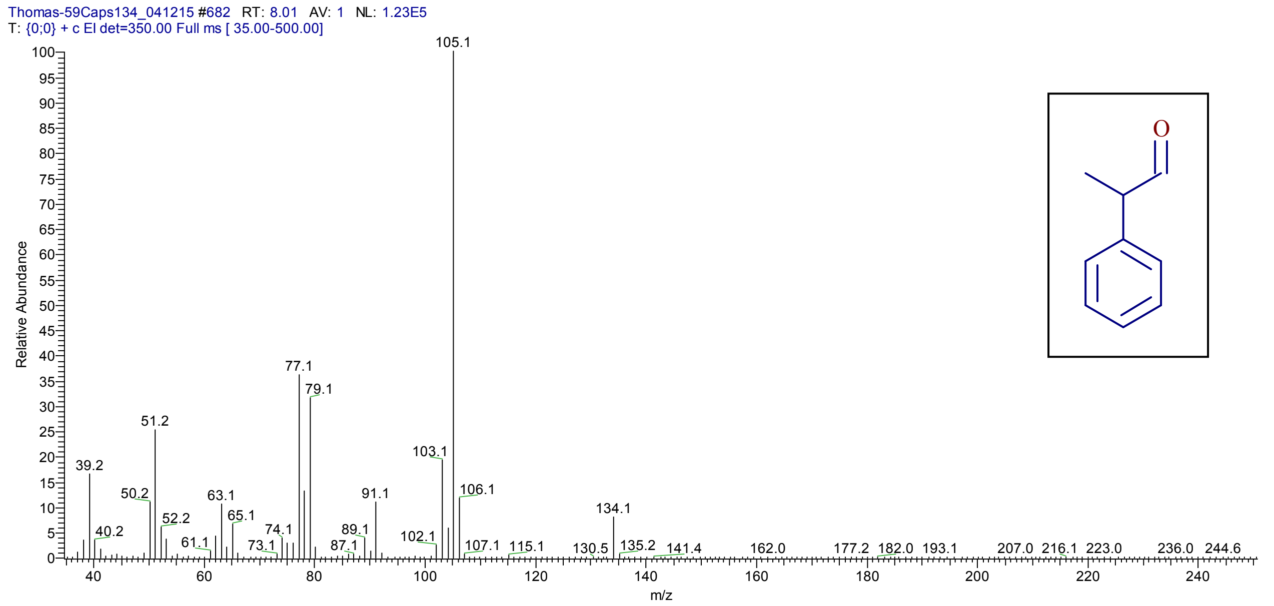
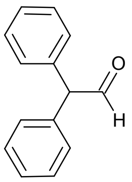


Figure 6. Mass spectrum of 2-phenylpropanal **3g**.

Diphenylacetaldehyde 3h



^{1}H NMR spectrum was in agreement with characterization already reported in the literature.[10]

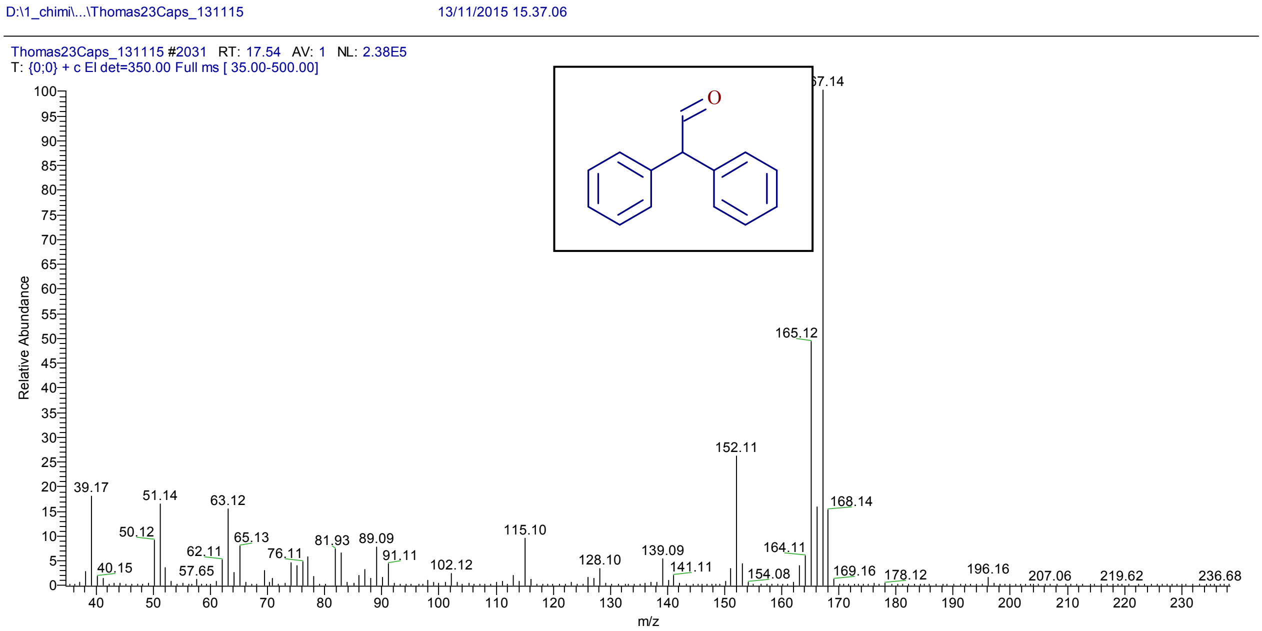
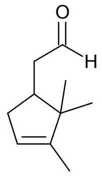


Figure 7. Mass spectrum of diphenylacetaldehyde **3h**.

(2,2,3-trimethylcyclopent-3-en-1-yl)acetaldehyde 3j



^{1}H NMR spectrum was in agreement with characterization already reported in the literature.[11]

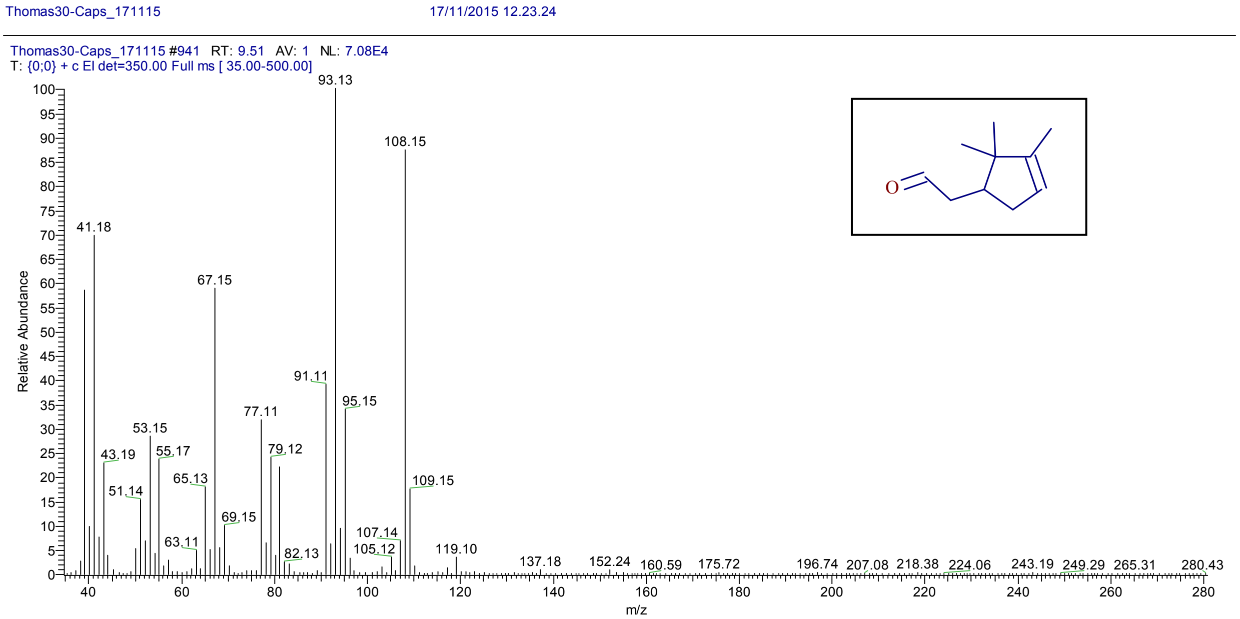
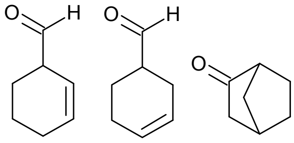
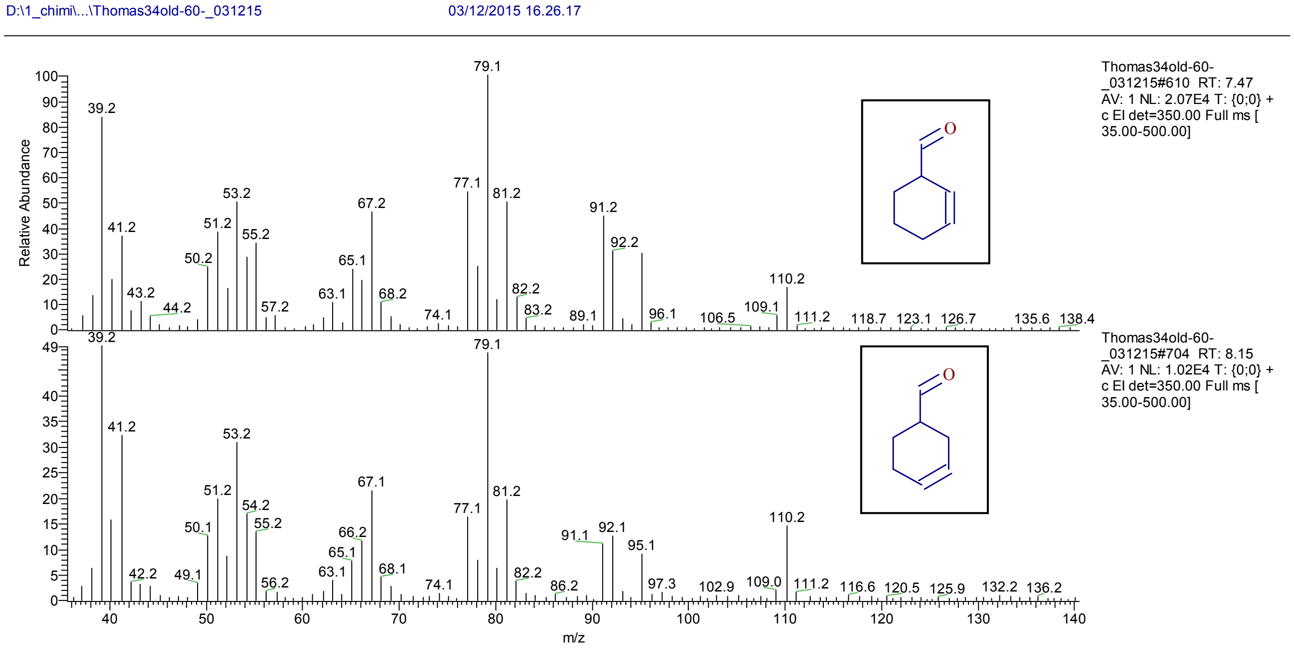


Figure 8. Mass spectrum of (2,2,3-trimethylcyclopent-3-en-1-yl)acetaldehyde **3j**.

cyclohex-2-ene-1-carbaldehyde 3k, cyclohex-3-ene-1-carbaldehyde 3k’ and bicyclo[2.2.1]heptan-2-one 3k’’



^{1}H NMR spectra were in agreement with characterization already reported in the literature.[12]



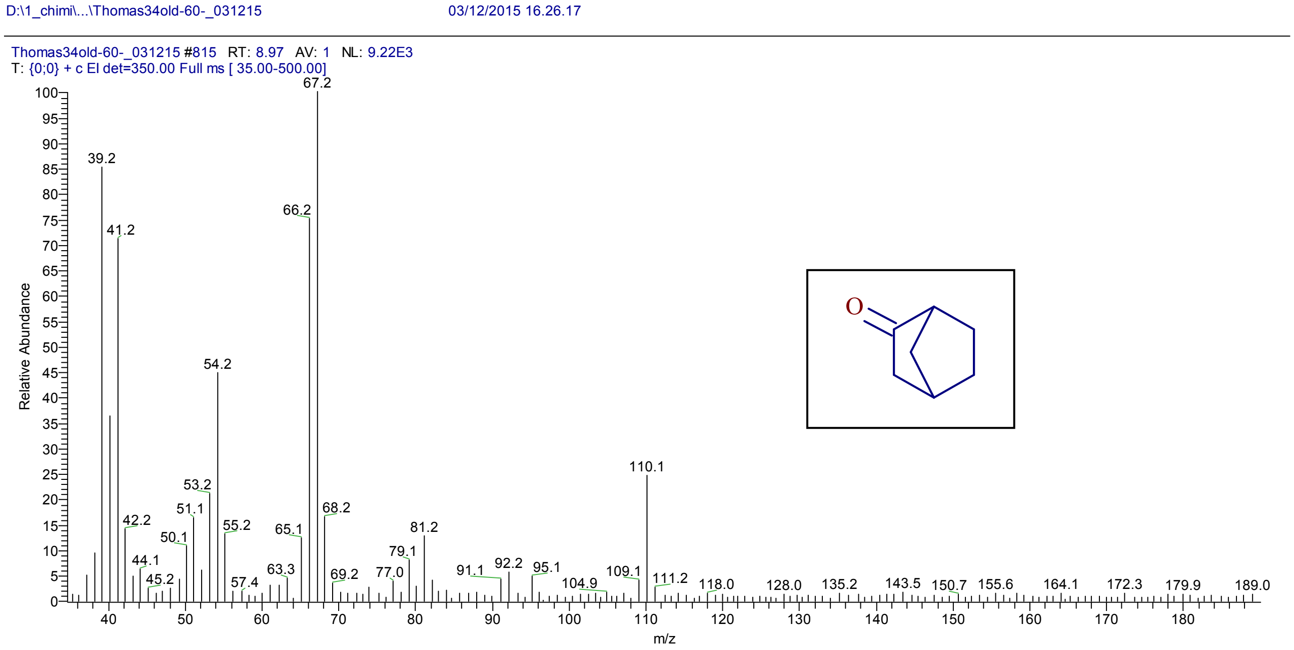
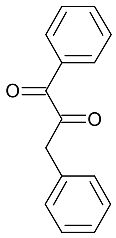


Figure 9. Mass spectra of cyclohex-2-ene-1-carbaldehyde **3k**, cyclohex-3-ene-1-carbaldehyde **3k’** and bicyclo[2.2.1]heptan-2-one **3k’’**.

1,3-diphenylpropane-1,2-dione 3l



^{1}H NMR spectrum was in agreement with characterization already reported in the literature.[13]

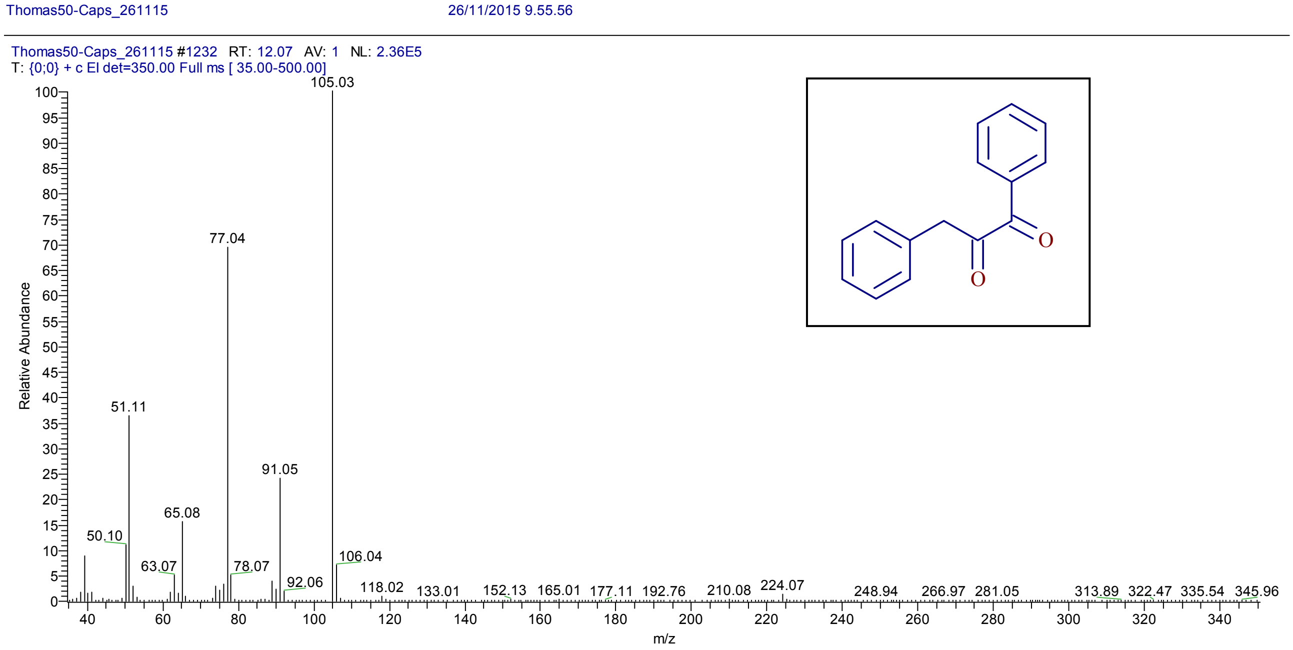
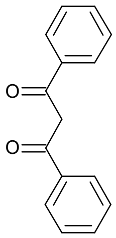


Figure 10. Mass spectrum of 1,3-diphenylpropane-1,2-dione **3l**.

1,3-diphenylpropane-1,3-dione 3l'



^{1}H NMR spectrum was in agreement with characterization already reported in the literature.[14]

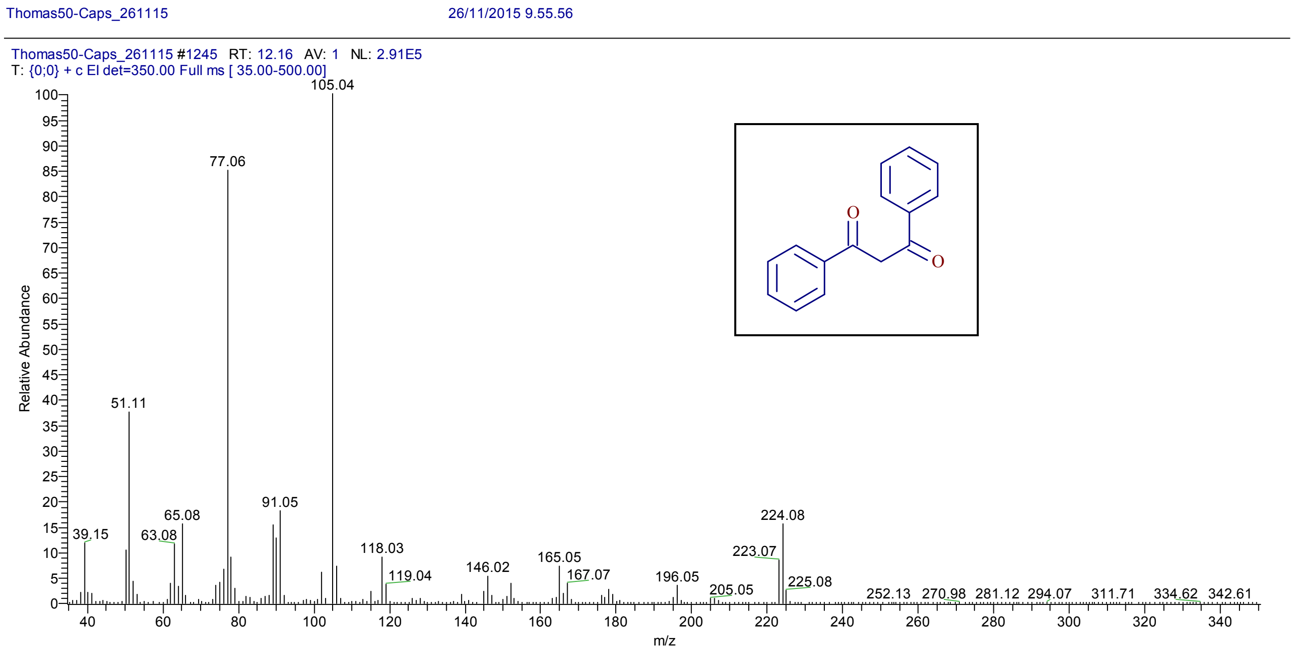


Figure 11. Mass spectrum of 1,3-diphenylpropane-1,3-dione **3l'**.

References

1 D.D. Perrin, W.L.F. Armarego, Purification of laboratory chemicals, 3rd edition, , Pergamon Press, 1993.

2 W. C. Still, M. Khan, A. Mitra *J. Org. Chem.* 1978, **43**, 2923-2925.

3 Y. Aoyama, Y. Tanaka, S. Sugahara, *J. Am. Chem. Soc.,* **1989**, *111*, 5397-5404.

4 C. Gaebert, J. Mattay, M. Toubartz, S. Steenken, B. Müller, T. Bally, *Chem. Eur. J.* **2005**, *11*, 1294-1304

5 S.K. Gupta, J. Choudhury, Chem. Commun. **2016,** *52***,** 3384-3387.

6 G.-Q. Chen, Z.-J. Xu, C.-Y. Zhou and C.-M. Che, *Chem. Commun*., **2011**, *47*, 10963-.

7 T. Pesnot, M.C. Gershater, J.M. Ward, H.C. Hailes, *Adv. Synth. Catal.* **2012** , *354*, 2997-3008.

8 M.A. Cinelli, H. Li, G. Chreifi, P. Martasek, L.J. Roman, T.L. Poulos, R.B. Silverman, *J. Med. Chem*. **2014**, *57*, 1513-1530.

9 C.A. Dutta; R. Ritwika; L.G. Kumar, *Chem. Commun.* **2012** , *48*, 5497-5499.

10 S. Renganathan, H. Soonsang, N. Ramalingam, Y. Minyoung, H. Raghunandan, K. Yonghwi, H.K. Young, K. Kimoon, *Chem. Commun.* **2012**, *48*, 11650-11652.

11 M.W.C. Robinson, K.S. Pillinger, I. Mabbett, D.A. Timms, A.E. Graham, *Tetrahedron*, **2010**, *66*, 8377-8382.

12 S. Munavalli, D. K. Rohrbaugh, H. D. Durst, *Phosph. Sulf. Silicon*, **2004**, *179*, 1657–1671.

13 C.-T. Chen, J.-Q. Kao, S.B. Salunke, Y.-H. Lin, *Org. Lett.* **2011**, *13*, 26-29.

14 C.-S. Kwan, A.S.C. Chan, K.C.-F. Leung, *Org. Lett.* **2016**, *18*, 976-979.