

Supporting Information

Non-symmetrical dialkyl carbonate synthesis promoted by 1-(3-trimethoxysilylpropyl)-3-methylimidazolium chloride

Subodh Kumar^a and Suman L. Jain^{a*}

^a Chemical Sciences Division, CSIR-Indian Institute of Petroleum, Dehradun-248005, India

Tel.: +91-135-2525788; Fax. +91-135-2660202;

Email: suman@iip.res.in

Contents

Instrumentation and Chemicals	S2
Experimental Procedure	S3-S4
FTIR & NMR spectra of Ionic Liquid 1	S5
¹ H, ¹³ C NMR and GC-MS of Products	S6-S22

Instrumentation and Chemicals

Dimethyl carbonate (DMC), *N*-methylimidazole (NMI), 3-chloropropyl trimethoxysilane (CPTMS), ionic liquids and alcohols were commercially available and were employed without further purification. All reactions were carried out under nitrogen atmosphere. ¹H and ¹³C NMR spectra were recorded at 500 MHz for CDCl₃ solutions. GC-MS (HP 5890, series II) analysis were carried out by using mass selective detector (MSD) (30m × 0.30 mm); 50-250 °C, 8 °C/min, and GC (GC, Agilent 6820) analysis was carried out using a silicon OV-17 column (50 m x 0.26); 50-250 °C, 5 min isothermal, 8 °C/min, FID 250 °C.

Experimental Procedure

Synthesis of 1-(3-trimethoxysilylpropyl)-3-methylimidazolium Chloride 1: A mixture of *N*-methylimidazole (20 ml, 25 mmol) and (3-chloropropyl) trimethoxysilane (6 g, 25 mmol) was heated at 110 °C for 36 h. The unreacted materials were washed by diethyl ether (8 ml × 3) and then the diethyl ether was removed under reduced pressure at room temperature. The resulting liquid was dried under reduced pressure at room temperature to yield a colorless ionic liquid **1**, isolated yield was 97%. IR (KBr): 1636, 1571, 1192, 1078, 1052 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ: 0.15 (2H, t, -CH₂-Si), 1.82 (2H, m, CH₂), 3.37 (9H, s, (-OCH₃)), 3.86 (3H, s, NCH₃), 4.02 (2H, t, -N-CH₂), 7.30 (1H, d, pr-H), 7.43 (1H, d, pr-H), 9.02 (1H, pr-H). ¹³C NMR (CDCl₃): 11.9, 36.6, 125.3, 127.4, 139.3.

General experimental procedure for transesterification of alcohol with DMC using ionic liquid 1: To a mixture of alcohol (5 mmol) and DMC (5 mmol) was added ionic liquid **1** (1 ml) and the resulting mixture was stirred at 80 °C. Progress of the reaction was monitored by TLC (SiO₂). After completion, the reaction mixture was cooled to room

temperature and the product was isolated by extraction with diethyl ether. The recovered ionic liquid was reused for recycling experiments. The organic layer was concentrated under reduced pressure and the obtained product was purified by column chromatography. The column was packed by slurry of silica gel and separation of product was done by using ethyl acetate/ hexane (4:6) as eluent. The products were analyzed by a gas chromatography and GC-MS and identity of the products was established by comparing their physical and spectral data with those of reported ones.

Experimental procedure of transesterification of 1-butanol with DMC using ionic liquids

3-6: To a mixture of 1-butanol (5 mmol) and DMC (5 mmol) was added ionic liquid (1 ml) and the resulting mixture was stirred at 80 °C. Progress of the reaction was monitored by TLC (SiO₂). After completion, the reaction mixture was cooled to room temperature and the product was isolated by extraction with diethyl ether. The organic layer was concentrated under reduced pressure and the obtained product was purified by column chromatography and then analyzed by GC-MS.

Experimental procedure of transesterification of 1-butanol with DMC using mixture of

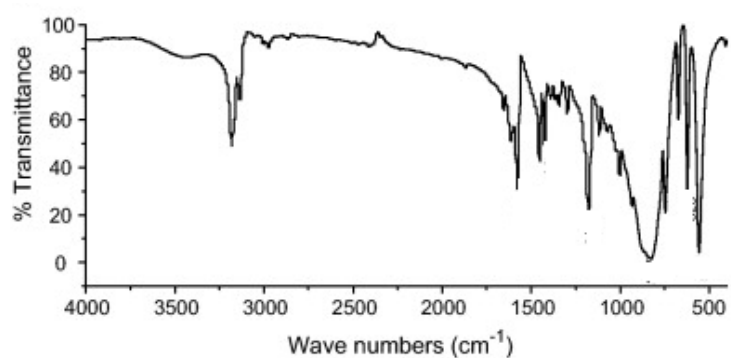
3-chloropropyl trimethoxysilane (CPTMS) and N-methyl imidazole (NMI): To a mixture of 1-butanol (5 mmol) and DMC (5 mmol) was added 1:1 mixture of CPTMS and NMI (1 ml) and the resulting mixture was stirred at 80 °C. Progress of the reaction was monitored by TLC (SiO₂). After completion, the reaction mixture was cooled to room temperature and was purified by column chromatography to obtain pure butyl methyl carbonate.

Reusability of ionic liquid IL 1.

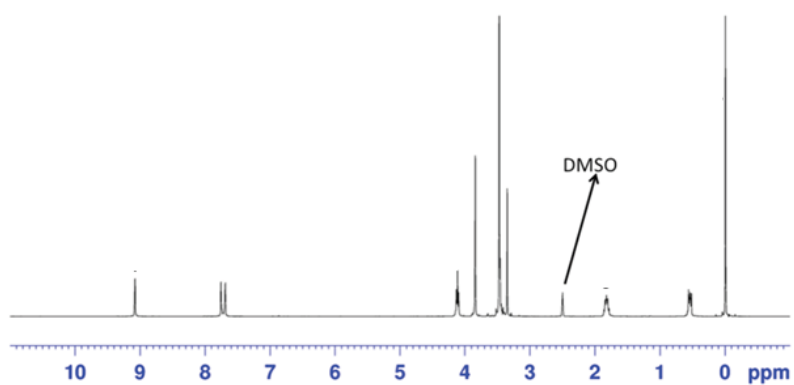
The reusability of **1** was examined by the reaction of DMC (5 mmol) and 1-butanol (5 mmol) at the optimized reaction conditions (80 °C, 4 h). After the reaction, the reaction

mixture was extracted with diethyl ether, which dissolves the reaction product and precipitated out the ionic liquid. The ionic liquid was dried under vacuum before its use for subsequent recycling experiment. The recovered ionic liquid reused for six runs. Tetradecane (10.0 mol% relative to the alcohol) was used as internal standard and the conversion (%) was calculated with respect to the alcohol. The reaction mixture was subjected to usual work-up to get the isolated yield of the butyl methyl carbonate.

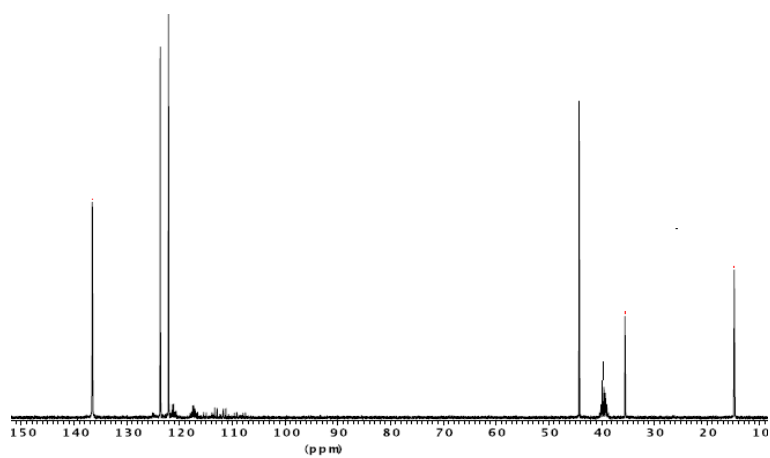
Characterization of the ionic liquid **1**



Supporting Fig. 1: FTIR Spectra of **1**



Supporting Fig. 2: ^1H NMR spectra of **1** in DMSO-D_6

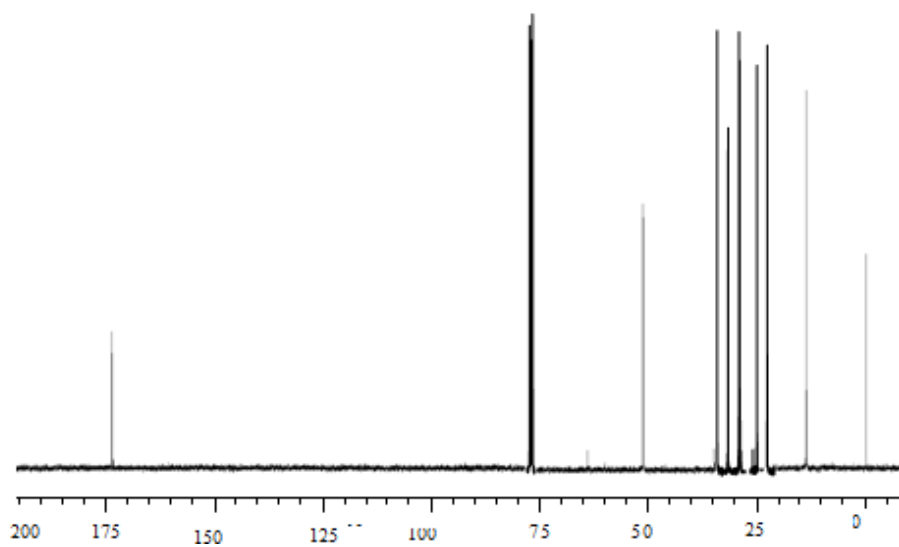
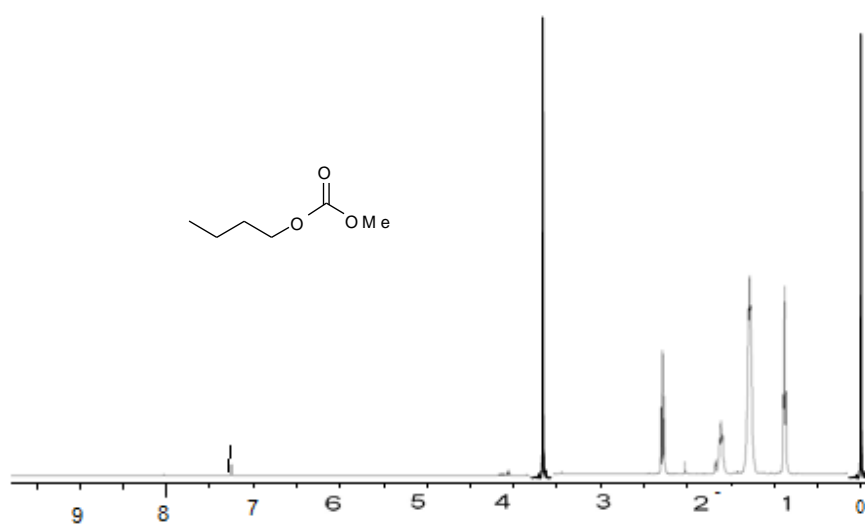


Supporting Fig. 3: ^{13}C NMR spectra of **1** in DMSO-D_6

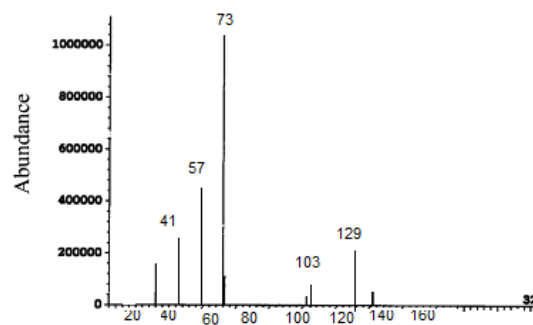
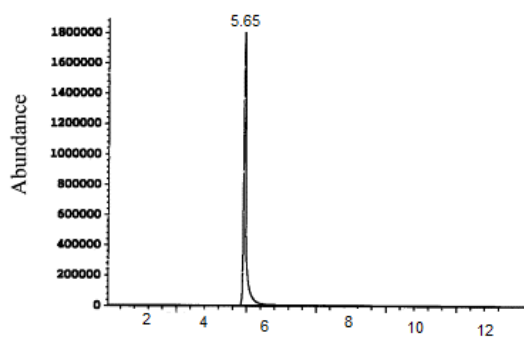
Supporting Table 1: GC-MS values of the products

Compound	GC/MS (EI, 70 eV)
Butyl methyl carbonate	m/z: 129 (M-2) ⁺ , 103 (M-CO) ⁺ , 73 ([M-COCH ₃] ⁺ , 57 ([M-OCOCH ₃] ⁺ , 41.
Pentyl methyl carbonate	m/z: 147 (M+1) ⁺ , 87 (M-OCOCH ₃) ⁺ , 71 (M-OCOCH ₃) ⁺ , 59 (OCOCH ₃) ⁺ , 42.
Hexyl methyl carbonate	m/z: 159 (M-1) ⁺ , 129 (M-OCH ₃) ⁺ , 101 (M-OCOCH ₃) ⁺ , 85 ([M-OCOOCH ₃] ⁺ , 57.
Octyl methyl carbonate	m/z: 175 (M+1) ⁺ , 143 (M-OCH ₃) ⁺ , 115 ([M-OCOCH ₃] ⁺ , 99 ([M-OCOCH ₃] ⁺ , 85 (C ₆ H ₁₃).
Cyclohexyl methyl carbonate	m/z: 99 (M-CH ₃ -CO ₂) ⁺ , 83 (M-CH ₃ OCO ₂) ⁺ , 82 (MCH ₃ OCO ₂ -H) ⁺ , 81, 77, 71, 67, 59.
Menthyl methyl carbonate	m/z: 139 (M-CH ₃ OCO ₂) ⁺ , 138 ([M-CH ₃ OCO ₂ -H] ⁺ , 123 ([M-CH ₃ OCO ₂ -CH ₄) ⁺ , 109 ([M-CH ₃ OCO ₂ -CH ₄ -CH ₂) ⁺ , 95 ([C ₇ H ₁₁] ⁺ , 81, 69 (12).
Benzyl methyl carbonate	m/z: 166 (M) ⁺ , 122 (M-CO ₂) ⁺ , 121 ([M-CO ₂ -H] ⁺ , 107 ([M-CO ₂ CH ₃) ⁺ , 91 ([C ₇ H ₇] ⁺ , 79 (30), 77.
4-Methylbenzyl methyl carbonate	m/z: 180 (M) ⁺ , 136 (M-CO ₂) ⁺ , 149 ([M-OCH ₃] ⁺ , 121 ([M-CO ₂ CH ₃) ⁺ , 105 ([C ₈ H ₉] ⁺ , 91.
4-Methoxybenzyl methyl carbonate	m/z: 196 (M) ⁺ , 152 (M-CO ₂) ⁺ , 151 ([M-CO ₂ -H] ⁺ , 137 ([M-CO ₂ CH ₃) ⁺ , 121 (M-OCOOCH ₃) ⁺ , 91 ([C ₇ H ₇] ⁺ , 77.
4-Chlorobenzyl methyl carbonate	m/z: 201 (M+1) ⁺ , 169 (M-OCH ₃) ⁺ , 156 (M-CO ₂) ⁺ , 153 [M-COOCH ₃] ⁺ , 125 ([M-OCOOCH ₃] ⁺ , 91 ([C ₇ H ₇] ⁺ .
Heptane 2-yl methyl carbonate	115(M-COOCH ₃) ⁺ , 99(C ₇ H ₁₅), 71 (C ₅ H ₁₁) ⁺
Methyl phenyl carbonate	152 (M) ⁺ , 108 (M-OCO), 93 (M-COCH ₃).
<i>p</i> -Tolyl methyl carbonate	166 (M) ⁺ , 139 (M-OCH ₃), 107 (M-COCH ₃), 91 (M-OCOCH ₃)

Table 1, entry 1



PP



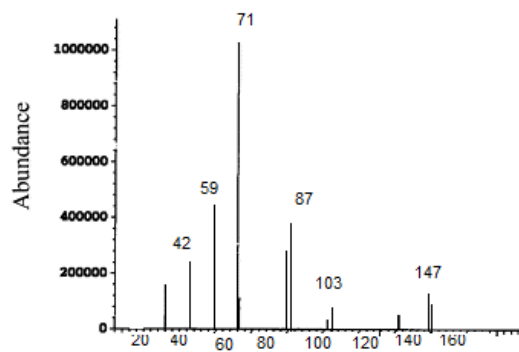
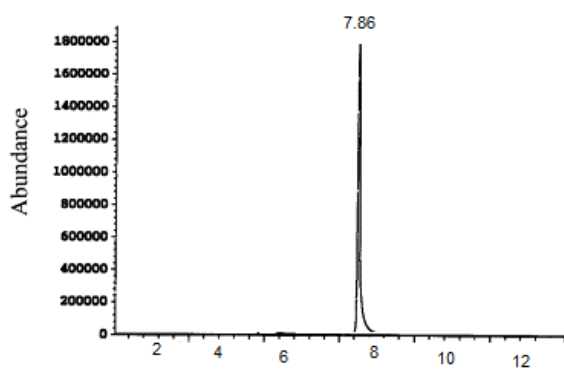
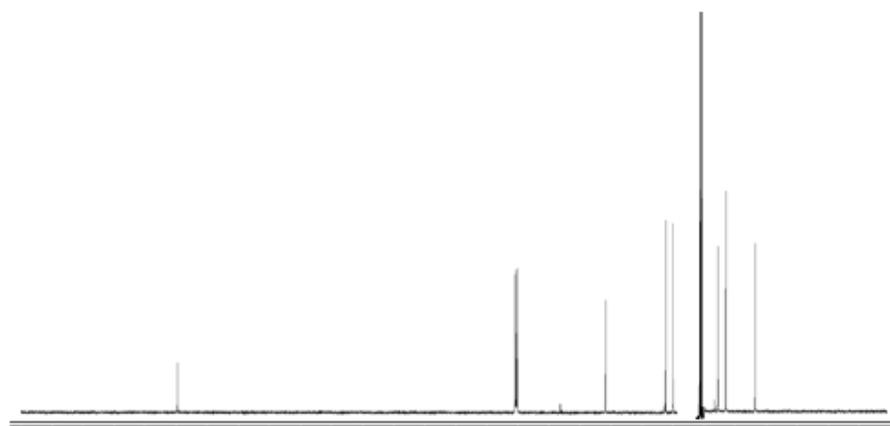
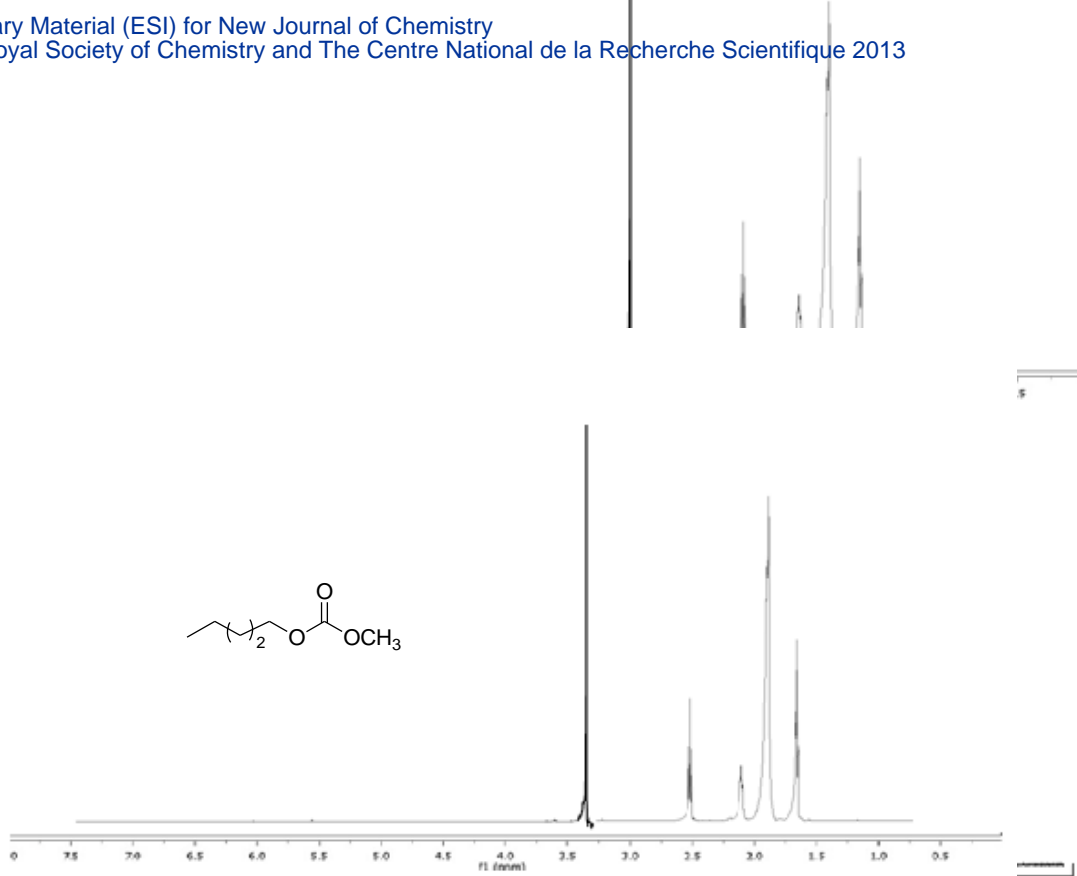


Table 1, entry 3:

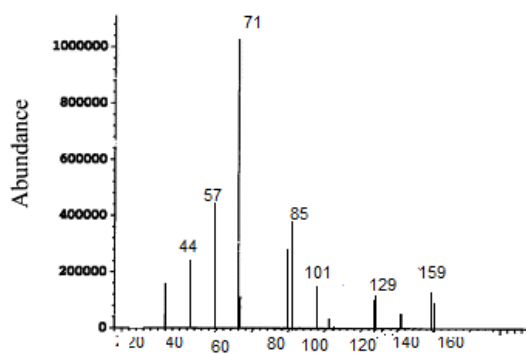
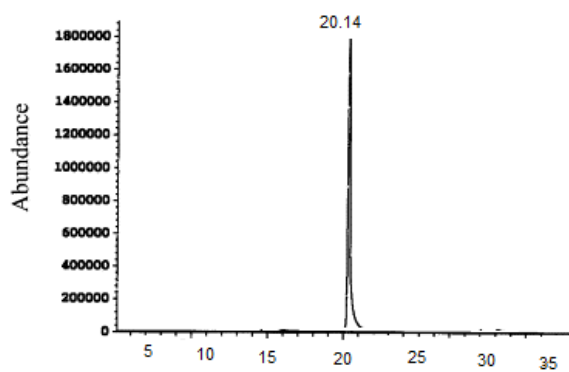
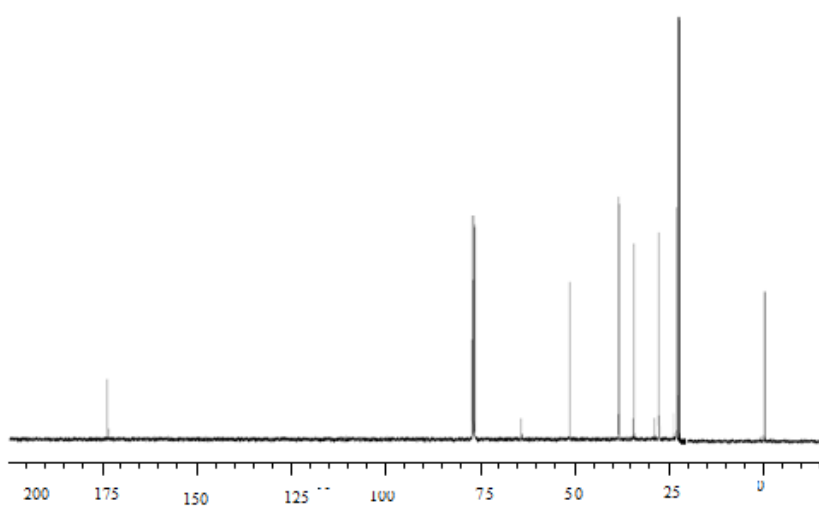
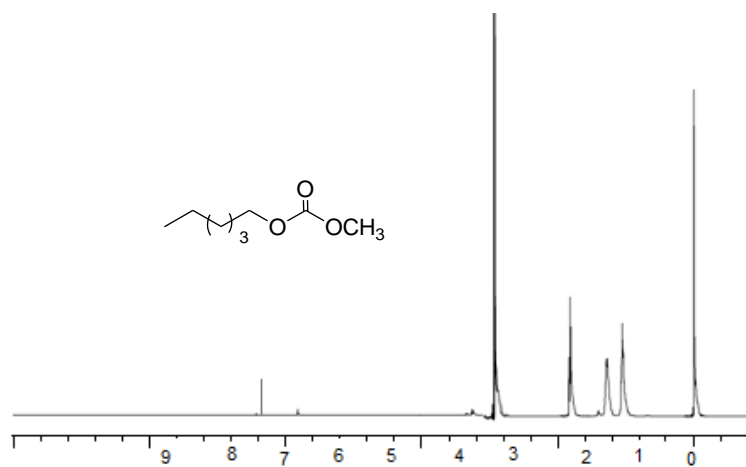


Table 1, entry 4

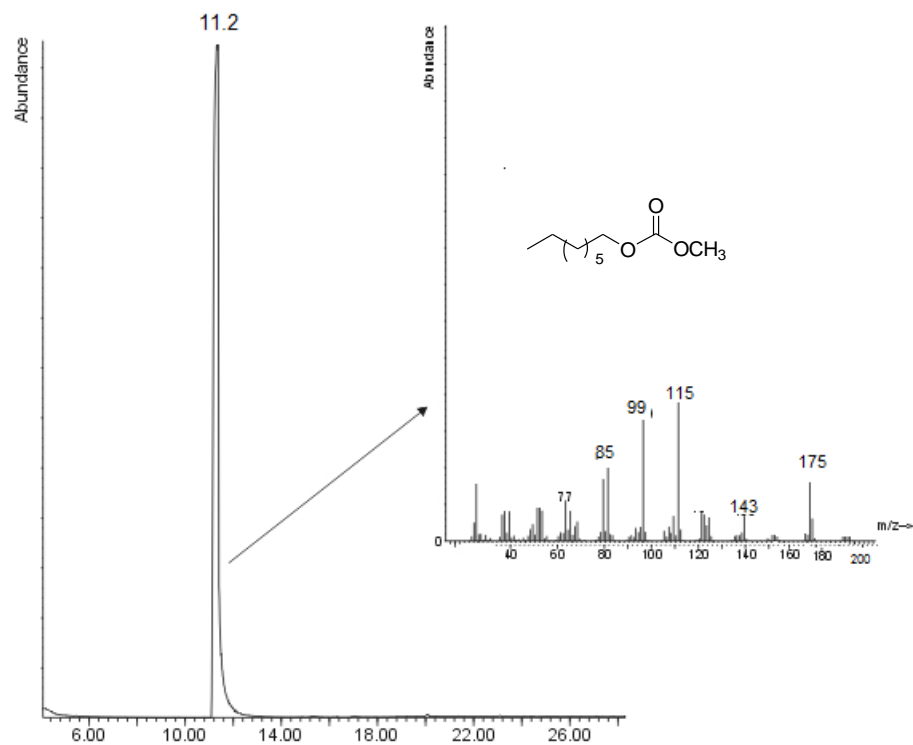


Table 1, entry 5

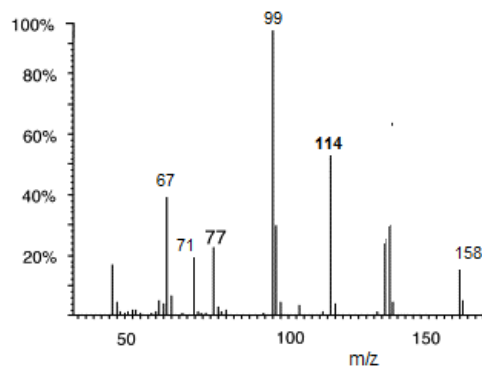
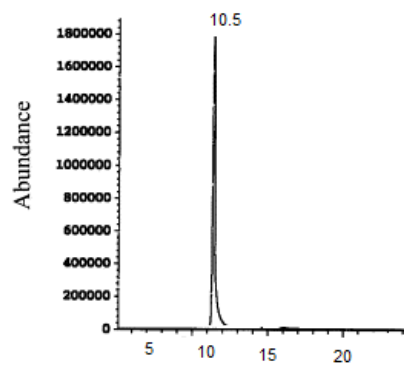
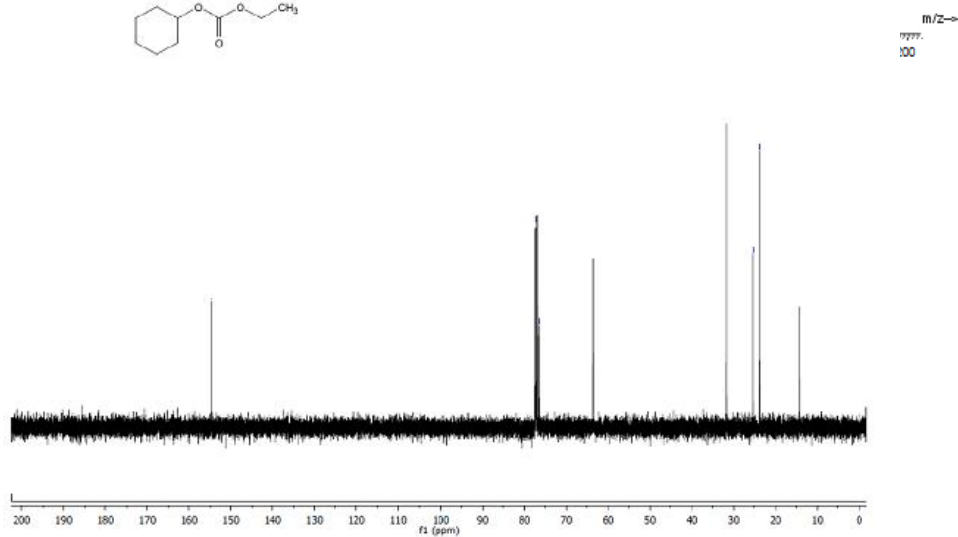
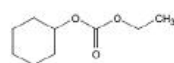
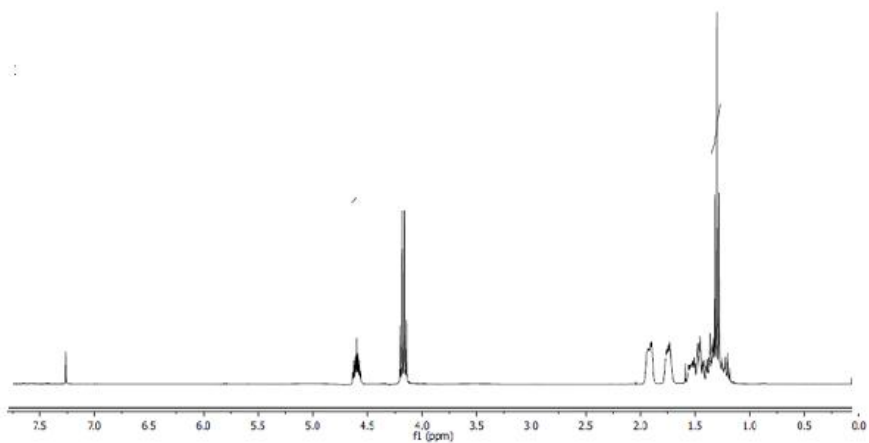
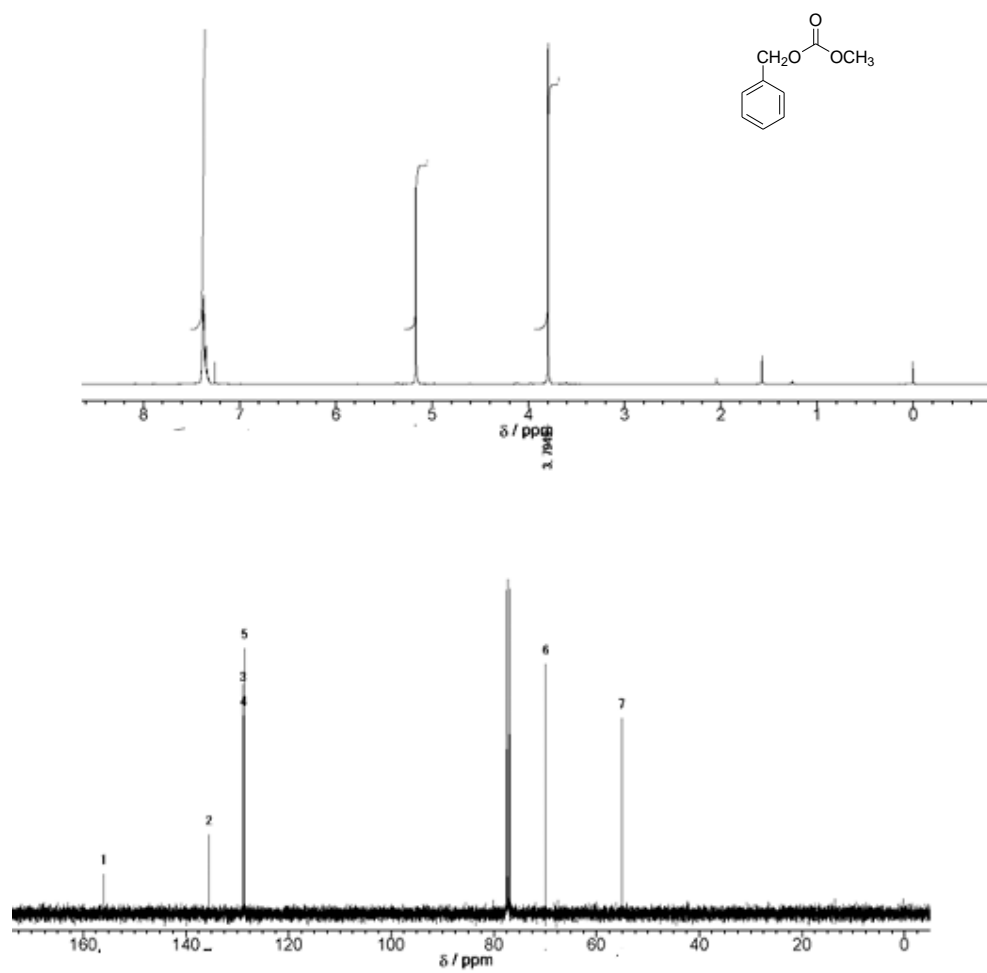


Table 1, entry 7



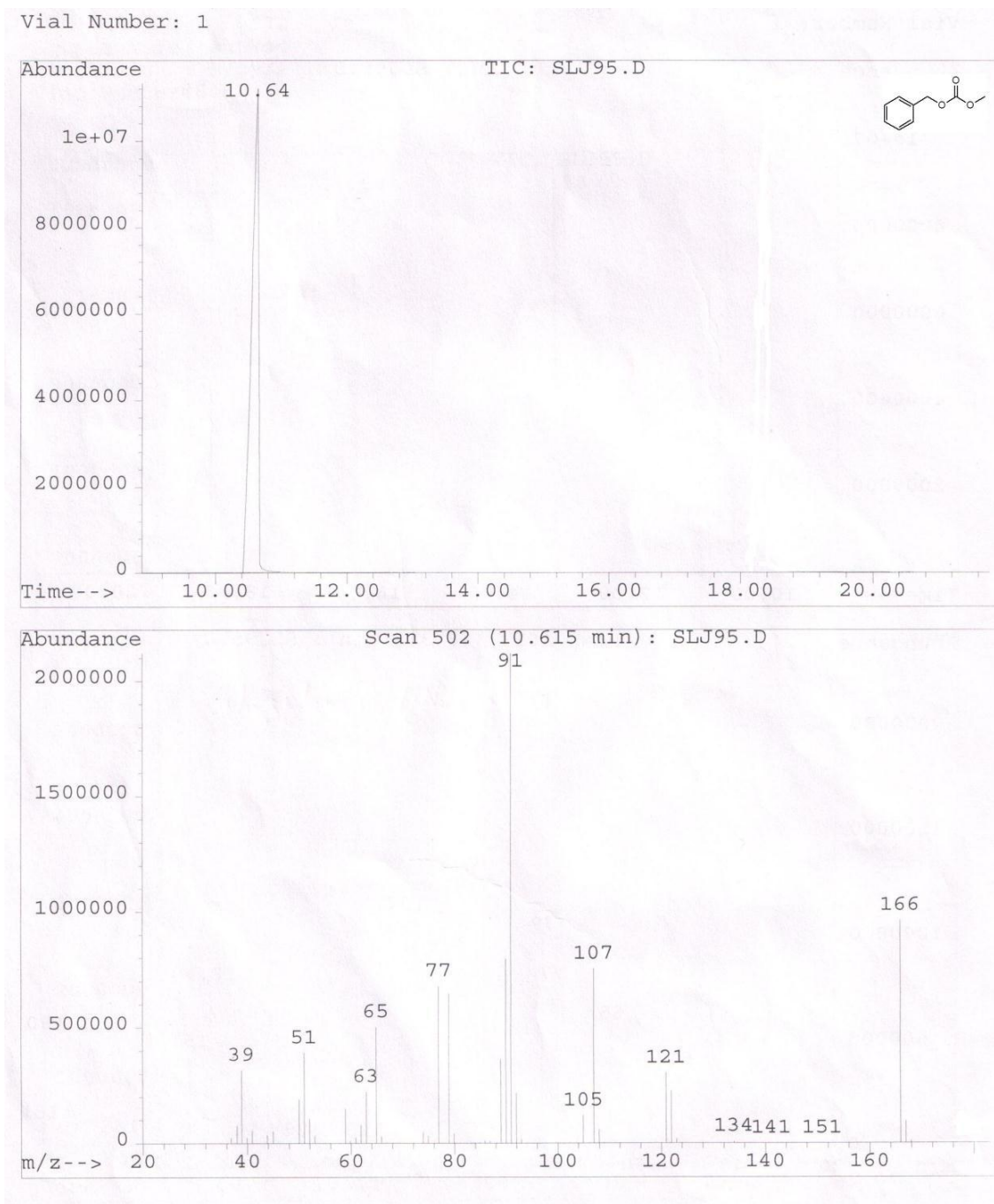


Table 1, entry 8:

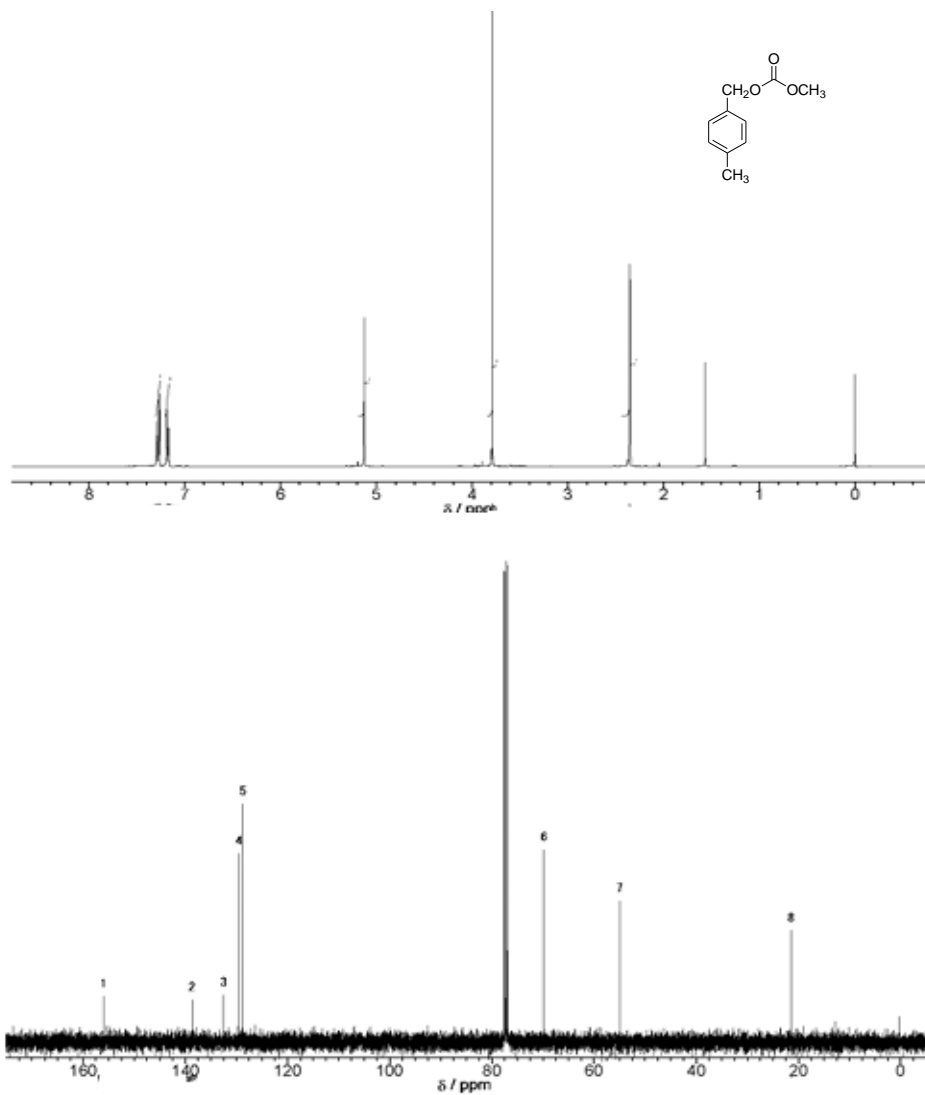
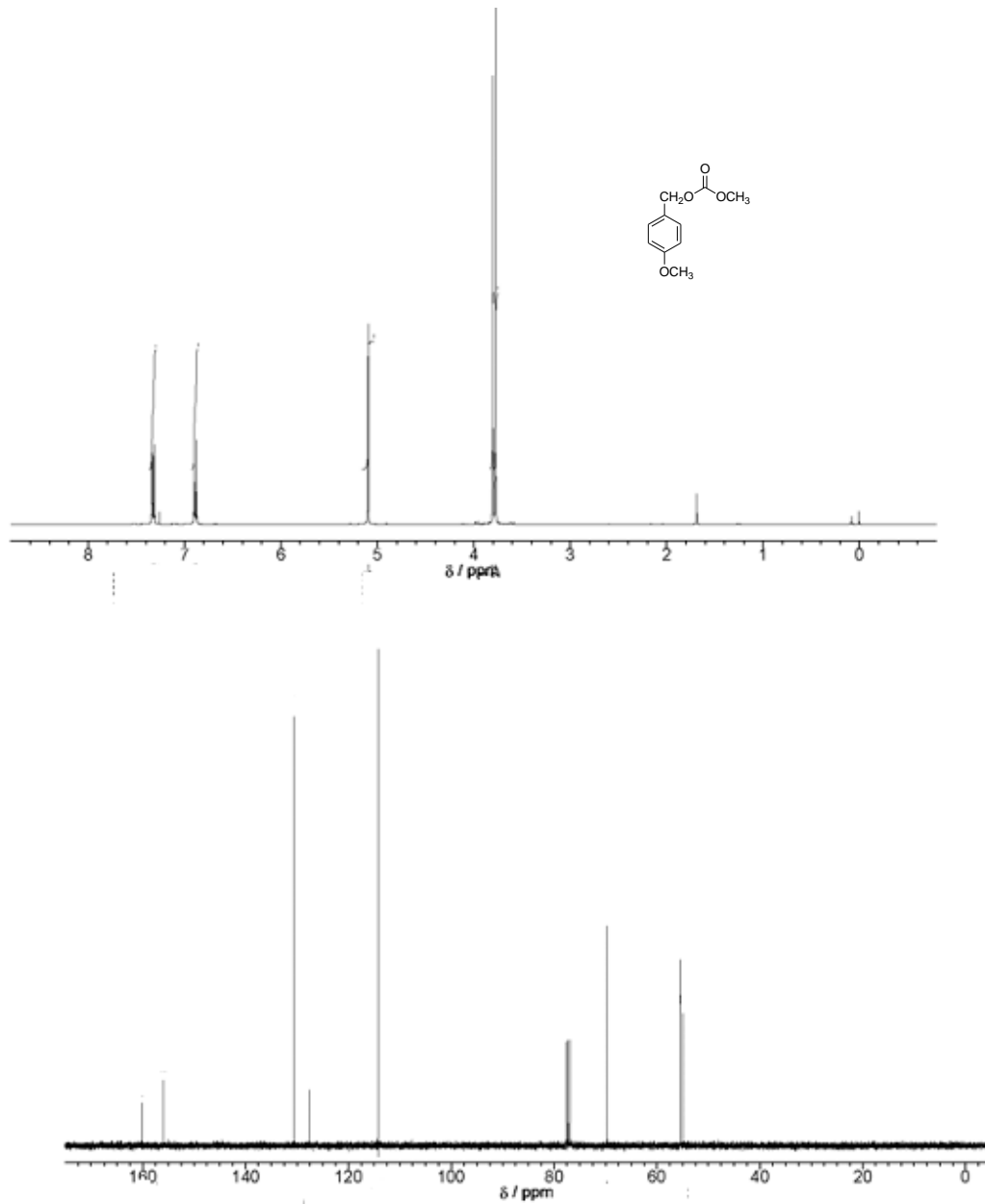


Table 1, entry 9:



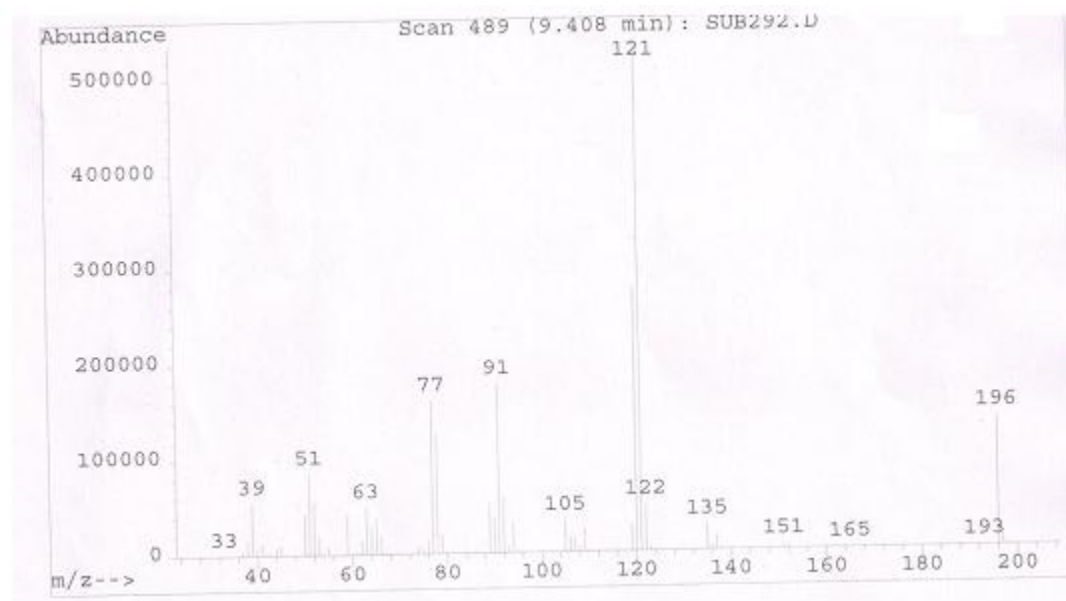
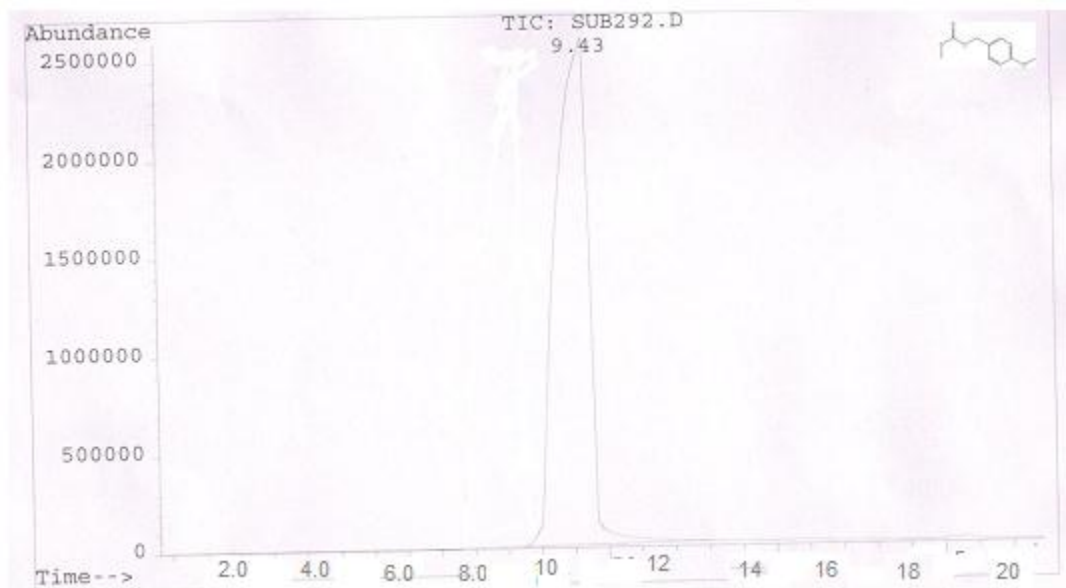
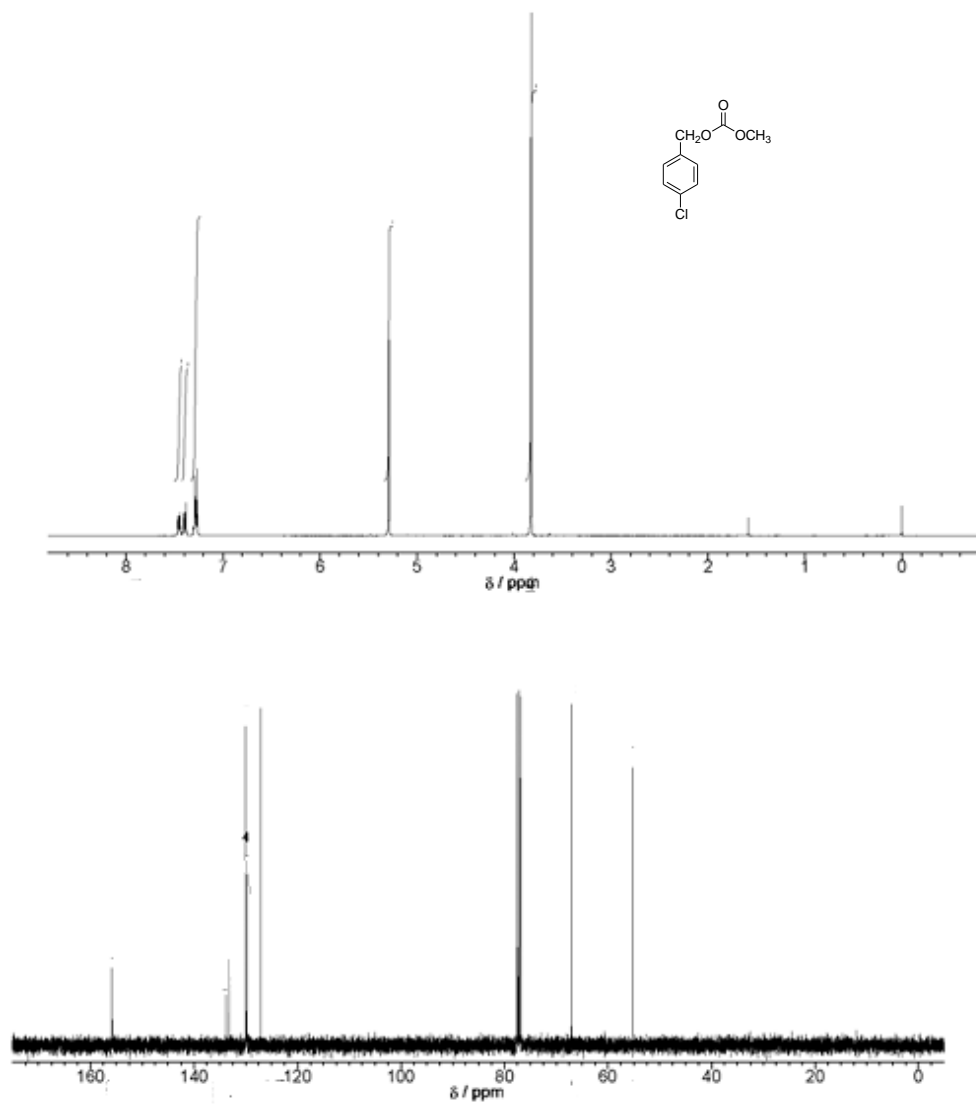


Table 1, entry 10:



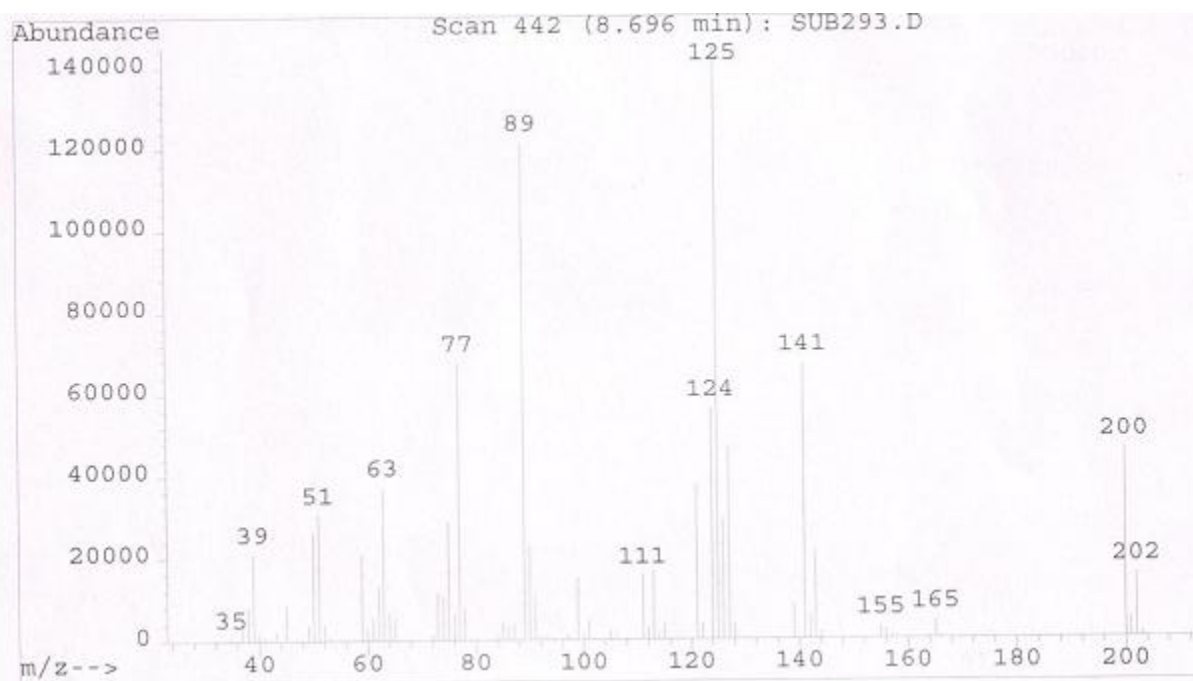
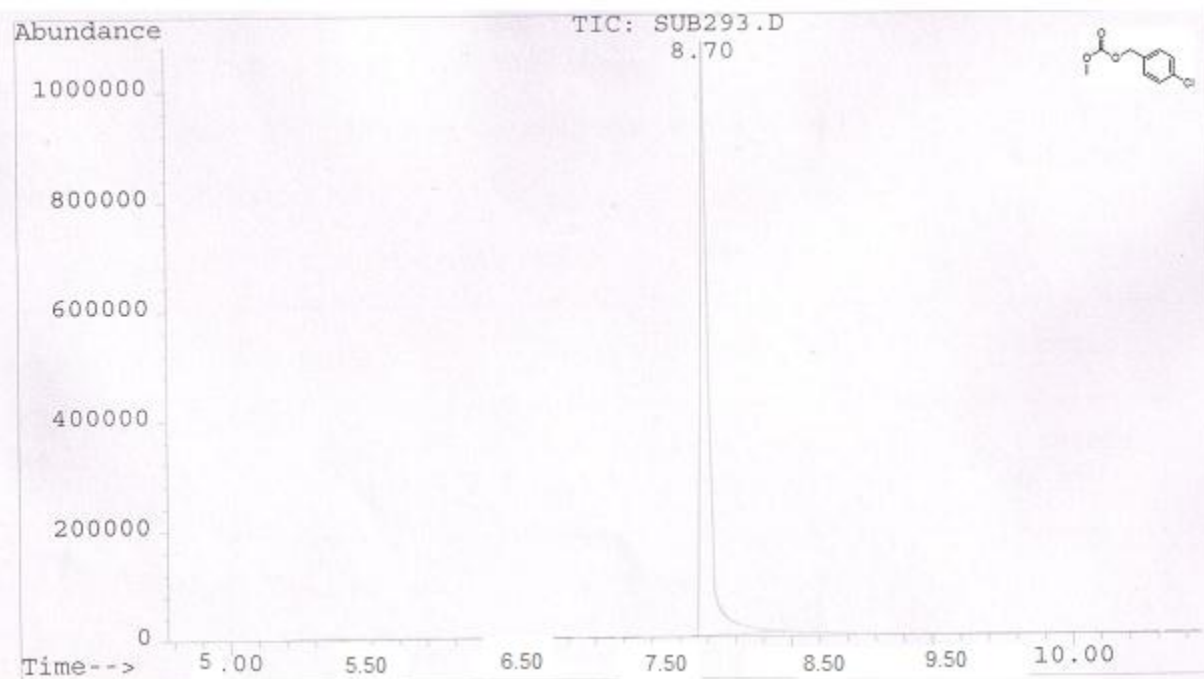


Table 1, entry 12

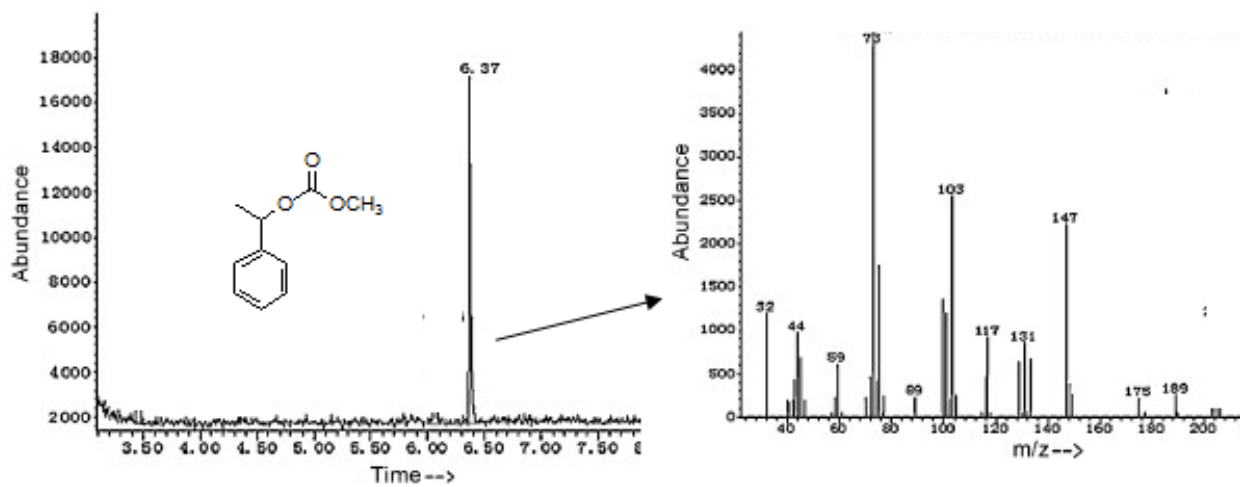


Table 1, entry 13

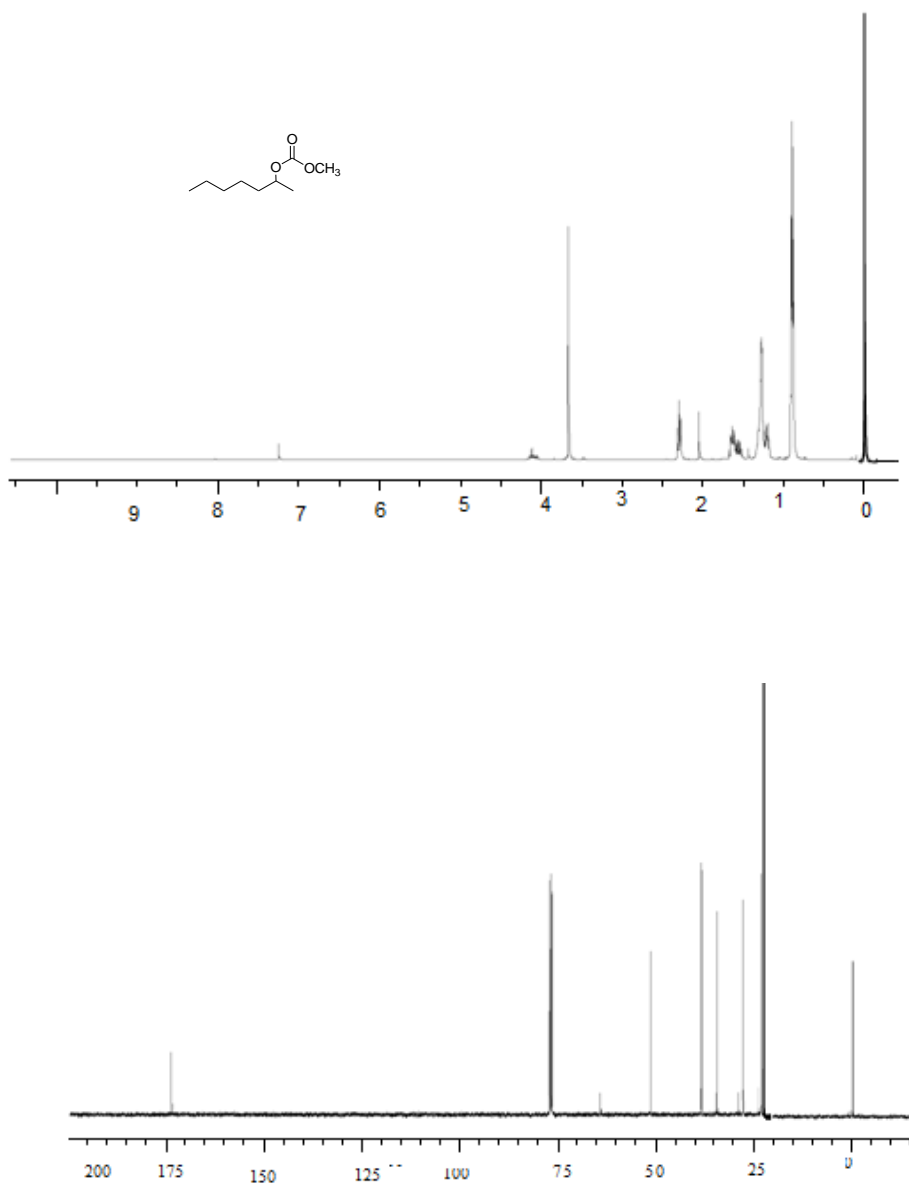
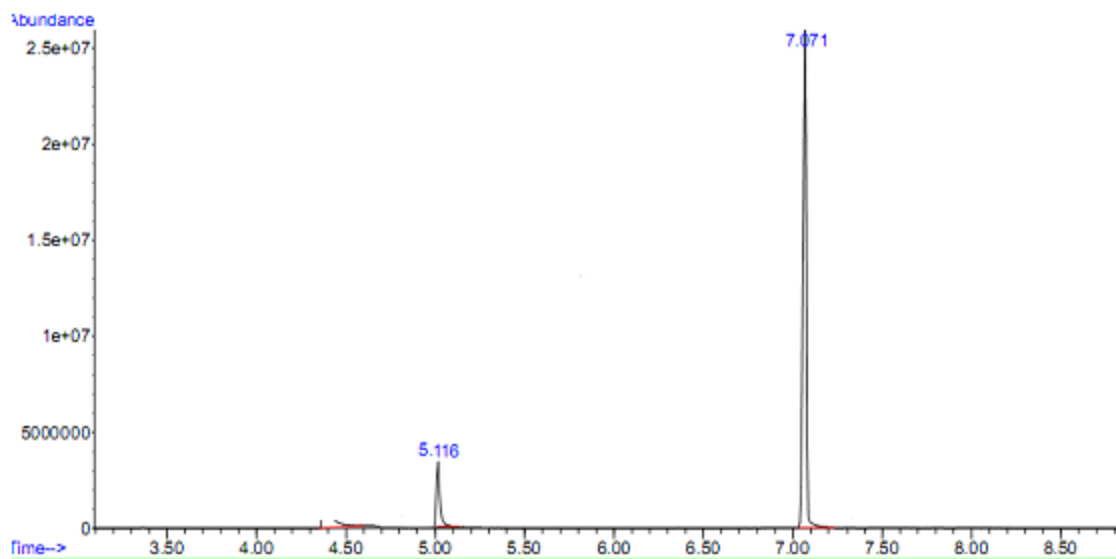
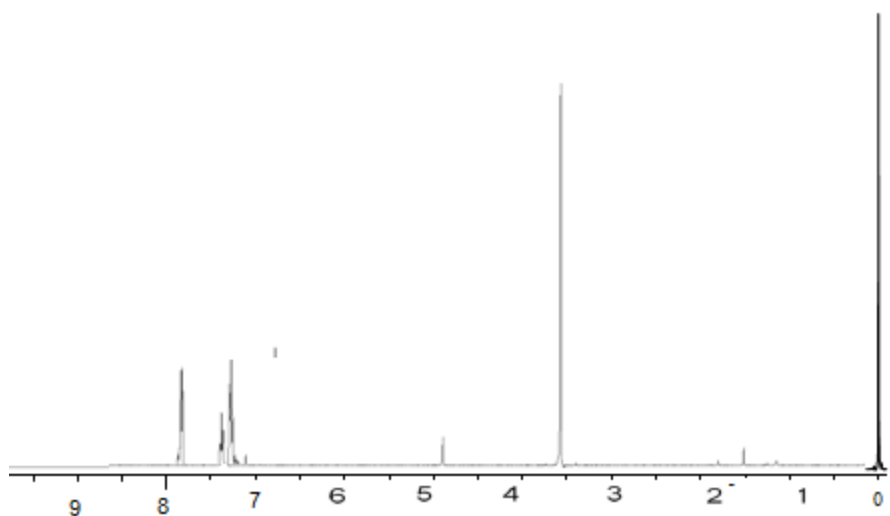
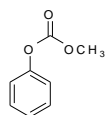


Table 1, entry 15



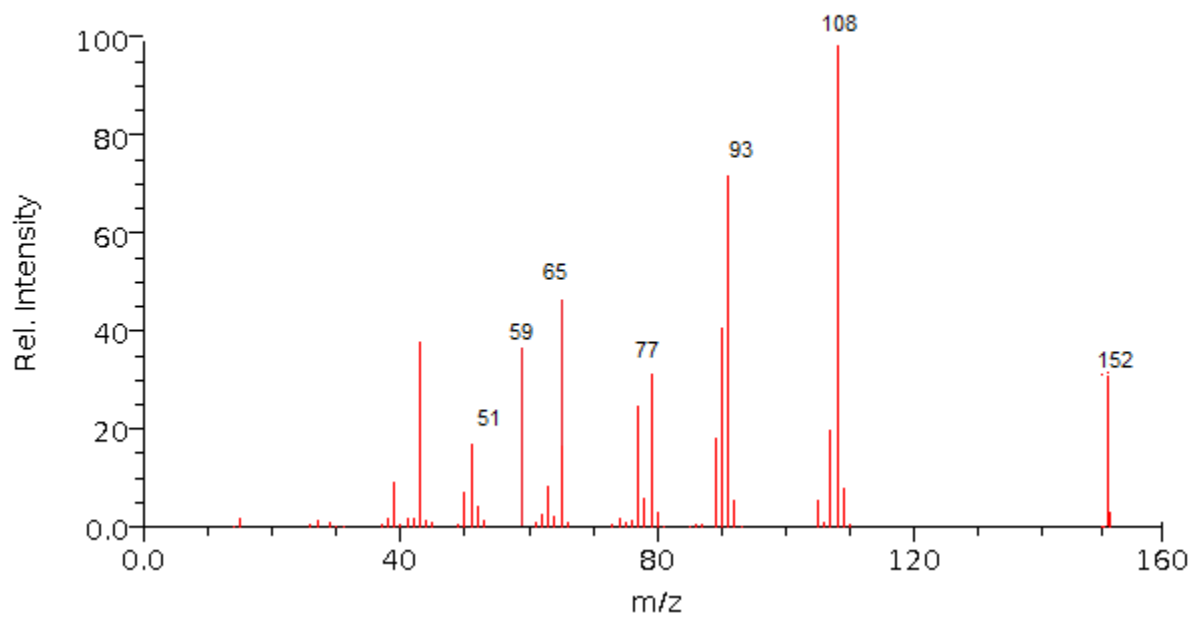


Table 1, entry 16

