

## CHAPTER IV

### RESULTS AND DISCUSSION

The chemical constituent of additives was analyzed by Infrared Spectrophotometry,  $^1\text{H}$ ,  $^{13}\text{C}$  Nuclear Magnetic Resonance Spectrometry and GLC-MS Spectroscopy. The gas chromatogram was analyzed by comparing the fragmentation ions patterns of mass spectra with these substances through a library search of GC-MS spectrometer (NIST database).

#### 4.1 Structural Elucidation of Base Oil

##### Exxon

ULT1 was obtained as colorless oil. Its IR-spectrum is shown in Fig. A1. The C-H stretching vibration peaks of an aliphatic compound were observed at 2957, 2926 and 2855  $\text{cm}^{-1}$ . The absorption peaks at 1463  $\text{cm}^{-1}$  and 1378  $\text{cm}^{-1}$  correspond to C-H symmetric bending vibration mode of  $-\text{CH}_3$  groups. In addition, the absorption peak at 724  $\text{cm}^{-1}$  might indicate the presence of one or more saturated long chain of  $-(\text{CH}_2)_n$ ;  $n > 4$ .

Table 4.1.1 The IR absorption band assignments of ULT1

Wavenumber ( $\text{cm}^{-1}$ )	Band type	Tentative assignment
2957, 2926, 2855	s	C-H stretching of $-\text{CH}_3, -\text{CH}_2-$
1463, 1378	m	C-H symmetric bending vibration of $-\text{CH}_3$
724	m	C-H rocking mode of $-\text{CH}_2-$ (for carbon > 4)

The  $^1\text{H}$ -NMR spectrum, Fig. A2, exhibited a signal at 0.9 ppm indicating the presence of protons attached to a methyl group. This was corroborated by the presence of the signal at 13.8 ppm in the  $^{13}\text{C}$ -NMR spectrum, Fig. A3. The signal for the interlinking methylene carbons were observed around 1.3 ppm in the  $^1\text{H}$ -NMR spectrum and 22.5-38.0 ppm in the  $^{13}\text{C}$ -NMR spectrum. The  $^1\text{H}$  NMR and  $^{13}\text{C}$ -NMR are summarized in Table 4.1.2.

Table 4.1.2 The  $^1\text{H}$  and  $^{13}\text{C}$ -NMR chemical shifts of ULT1

$^1\text{H}$ (ppm)	$^{13}\text{C}$ (ppm)	IR ( $\text{cm}^{-1}$ )	Tentative assignment
0.9	13.8	1463, 1378	$-\text{CH}_3$
1.3	22.5-38.0	724	$-(\text{CH}_2)_n-$

The gas chromatogram displayed peaks at retention times (Rt) 7.378 and 19.121 to 30.860 min (Fig. A4). The fragmentation ions patterns of ULT1 at Rt 7.378 and 19.121 to 30.860 min were similar to butylated hydroxytoluene (Fig. A5) and long chain saturated hydrocarbon (Fig. A6).

However, the identity of these compounds ought to be confirmed by comparing with an authentic sample.

The composition of compounds contained in ULT1 are presented in Table 4.1.3.

Table 4.1.3 The compounds contained in ULT1

Rt (min)	Name
7.378	butylated hydroxytoluene
19.121 to 30.860	long chain saturated hydrocarbon

#### Shell

TMO1 was obtained as colorless oil. Its IR-spectrum is shown in Fig. A7. The C-H stretching vibration peaks of an aliphatic compound were observed at 2920 and 2820  $\text{cm}^{-1}$ . The absorption peaks at 1460  $\text{cm}^{-1}$  and 1370  $\text{cm}^{-1}$  correspond to C-H symmetric bending vibration mode of  $-\text{CH}_3$  groups. In addition, the absorption peak at 720  $\text{cm}^{-1}$  might indicate the presence of one or more saturated long chain of  $-(\text{CH}_2)_n-$ ;  $n > 4$ .



Table 4.1.4 The IR absorption band assignments of TMOI

Wavenumber ( $\text{cm}^{-1}$ )	Band type	Tentative assignment
2920, 2820	s	C-H stretching vibration of $-\text{CH}_3, -\text{CH}_2-$
1460, 1370	m	C-H symmetric bending vibration of $-\text{CH}_3$
720	m	C-H rocking mode of $-\text{CH}_2-$ (for carbon $>$ 4)

The  $^1\text{H}$ -NMR spectrum, Fig. A8, exhibited a signal at 0.9 ppm indicating the presence of protons attached to a methyl group. This was corroborated by the presence of the signal at 14.0 ppm in the  $^{13}\text{C}$ -NMR spectrum., Fig. A9. The signal for the interlinking methylene carbons were observed around 1.3 ppm in the  $^1\text{H}$ -NMR spectrum and 22.0-36.0 ppm in the  $^{13}\text{C}$ -NMR spectrum. The  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR are summarized in Table 4.1.5.

Table 4.1.5 The  $^1\text{H}$  and  $^{13}\text{C}$ -NMR chemical shifts of TMOI

$^1\text{H}$ (ppm)	$^{13}\text{C}$ (ppm)	IR ( $\text{cm}^{-1}$ )	Tentative assignment
0.9	14.0	1460, 1370	$-\text{CH}_3$
1.3	22.0-36.0	720	$-(\text{CH}_2)_n-$

The gas chromatogram displayed peaks at retention times (Rt) 7.378 and 10.556 to 30.771 min (Fig. A10). The fragmentation ions patterns of TMO1 at Rt 7.378 and 10.556 to 30.771 min were similar to butylated hydroxytoluene (Fig. A11) and long chain saturated hydrocarbon (Fig. A12).

However, the identity of these compounds ought to be confirmed by comparing with an authentic sample.

The composition of compounds contained in TMO1 is presented in Table 4.1.6

Table 4.1.6 The compounds contained in TMO1

Rt (min)	Name
7.378	butylated hydroxytoluene
10.556 to 30.771	long chain saturated hydrocarbon

### BP

BP1 was obtained as colorless oil. Its IR-spectrum is shown in Fig. A13. The C-H stretching vibration peaks of an aliphatic compound were observed at 2920 and 2860  $\text{cm}^{-1}$ . The absorption peaks at 1460  $\text{cm}^{-1}$  and 1380  $\text{cm}^{-1}$  correspond to C-H symmetric bending vibration mode of  $\text{CH}_3$  groups. In addition, the absorption peak at 720  $\text{cm}^{-1}$  might indicate the presence of one or more saturated long chain of  $-(\text{CH}_2)_n$ ;  $n > 4$ .

Table 4.1.7 The IR absorption band assignments of BP1

Wavenumber ( $\text{cm}^{-1}$ )	Band type	Tentative assignment
2920, 2860	s	C-H stretching vibration of $-\text{CH}_3, -\text{CH}_2-$
1460, 1380	m	C-H symmetric bending vibration of $-\text{CH}_3$
720	m	C-H rocking mode of $-\text{CH}_2-$ (for carbon $>4$ )

The  $^1\text{H}$ -NMR spectrum, Fig. A14, exhibited a signal at 0.9 ppm indicating the presence of protons attached to a methyl group. This was corroborated by the presence of the signal at 14.6 ppm in the  $^{13}\text{C}$ -NMR spectrum. (Fig A15). The signal for the interlinking methylene carbons were observed around 1.5 ppm in the  $^1\text{H}$ -NMR spectrum and 23.0-37.0 ppm in the  $^{13}\text{C}$ -NMR spectrum. The  $^1\text{H}$  NMR and  $^{13}\text{C}$ -NMR are summarized in Table 4.1.8

Table 4.1.8 The  $^1\text{H}$  and  $^{13}\text{C}$ -NMR chemical shifts of BP1

$^1\text{H}$ (ppm)	$^{13}\text{C}$ (ppm)	IR ( $\text{cm}^{-1}$ )	Tentative assignment
1.2	14.6	1460, 1380	$-\text{CH}_3$
1.5	23.0-37.0	720	$-(\text{CH}_2)_n-$



The gas chromatogram displayed peaks at retention times (Rt) 7.421 and 18.425 to 30.795 min (Fig. A16). The fragmentation ions patterns of BP1 at Rt 7.421 and 18.425 to 30.795 min were similar to butylated hydroxytoluene (Fig. A17) and long chain saturated hydrocarbon (Fig. A18).

However, the identity of these compounds ought to be confirmed by comparing with an authentic sample.

The composition of compounds contained in BP1 are presented in Table 4.1.9.

Table 4.1.9 The compounds contained in BP1

Rt (min)	Name
7.421	butylated hydroxytoluene
18.425 to 30.795	long chain saturated hydrocarbon

#### Castrol

CAS1 was obtained as colorless oil. Its IR-spectrum is shown in Fig. A19. The C-H stretching vibration peaks of an aliphatic compound were observed at 2960, 2940 and 2860  $\text{cm}^{-1}$ . The absorption peaks at 1450  $\text{cm}^{-1}$  and 1380  $\text{cm}^{-1}$  correspond to C-H symmetric bending vibration mode of  $-\text{CH}_3$  groups. In addition, the absorption peak at 720  $\text{cm}^{-1}$  might indicate the presence of one or more saturated long chain of  $-(\text{CH}_2)_n-$ ;  $n > 4$ .

Table 4.1.10 The IR absorption band assignments of CAS1

Wavenumber ( $\text{cm}^{-1}$ )	Band type	Tentative assignment
2960, 2940, 2860	s	C-H stretching of $-\text{CH}_3, -\text{CH}_2-$
1450, 1380	m	C-H symmetric bending vibration of $-\text{CH}_3$
720	m	C-H rocking mode of $-\text{CH}_2-$ (for carbon $>$ 4)

The  $^1\text{H}$ -NMR spectrum, Fig. A20, exhibited a signal at 0.9 ppm indicating the presence of protons attached to a methyl group. This was corroborated by the presence of the signal at 14.3 ppm in the  $^{13}\text{C}$ -NMR spectrum, Fig. A21. The signal for the interlinking methylene carbons were observed around 1.3 ppm in the  $^1\text{H}$ -NMR spectrum and 23.0-32.1 ppm in the  $^{13}\text{C}$ -NMR spectrum. The  $^1\text{H}$  NMR and  $^{13}\text{C}$ -NMR are summarized in Table 4.1.11.

Table 4.1.11 The  $^1\text{H}$  and  $^{13}\text{C}$ -NMR chemical shifts of CAS2

$^1\text{H}$ (ppm)	$^{13}\text{C}$ (ppm)	IR ( $\text{cm}^{-1}$ )	Tentative assignment
0.9	14.3	1450, 1380	$-\text{CH}_3$
1.3	23.0-32.1	720	$-(\text{CH}_2)_n-$



The gas chromatogram displayed peaks at retention times (Rt) 7.401 and 18.419 to 30.000 min (Fig. A22). The fragmentation ions patterns of CAS1 at Rt 7.401 and 18.419 to 30.000 min were similar to butylated hydroxytoluene (Fig. A23) and long chain saturated hydrocarbon (Fig. A24).

However, the identity of these compounds ought to be confirmed by comparing with an authentic sample.

The composition of compounds contained in CAS1 are presented in Table 4.1.12.

Table 4.1.12 The compounds contained in CAS1

Rt (min)	Name
7.378	butylated hydroxytoluene
18.419 to 30.000	long chain saturated hydrocarbon

#### Mobil

MOB1 was obtained as colorless oil. Its IR-spectrum is shown in Fig. A25. The C-H stretching vibration peaks of an aliphatic compound were observed at 2960, 2920 and 2850  $\text{cm}^{-1}$ . The absorption peaks at 1460  $\text{cm}^{-1}$  and 1380  $\text{cm}^{-1}$  correspond to C-H symmetric bending vibration mode of  $-\text{CH}_3$  groups. In addition, the absorption peak at 720  $\text{cm}^{-1}$  might indicate the presence of one or more saturated long chain of  $-(\text{CH}_2)_n$   $n > 4$ .

Table 4.1.13 The IR absorption band assignments of MOB1

Wavenumber ( $\text{cm}^{-1}$ )	Band type	Tentative assignment
2960, 2920, 2850	s	C-H stretching of $-\text{CH}_3$ , $-\text{CH}_2-$
1460, 1380	m	C-H symmetric bending vibration of $\text{CH}_3$
720	m	C-H rocking mode of $-\text{CH}_2-$ (for carbon $>4$ ).

The  $^1\text{H}$ -NMR spectrum, Fig. A26, exhibited a signal at 0.9 ppm indicating the presence of protons attached to a methyl group. This was corroborated by the presence of the signal at 14.3 ppm in the  $^{13}\text{C}$ -NMR spectrum (Fig. A27). The signal for the interlinking methylene carbons were observed around 1.3 ppm in the  $^1\text{H}$ -NMR spectrum and 22.9-37.3 ppm in the  $^{13}\text{C}$ -NMR spectrum. The  $^1\text{H}$  NMR and  $^{13}\text{C}$ -NMR are summarized in Table 4.1.14

Table 4.1.14 The  $^1\text{H}$  and  $^{13}\text{C}$ -NMR chemical shifts of MOB1.

$^1\text{H}$ (ppm)	$^{13}\text{C}$ (ppm)	IR ( $\text{cm}^{-1}$ )	Tentative assignment
0.9	14.3	1460, 1380	$-\text{CH}_3$
1.3	22.9-37.3	720	$-(\text{CH}_2)_n-$

The gas chromatogram displayed peaks at retention times (Rt) 7.391 and 8.935 to 31.838 min (Fig. A28). The fragmentation ions patterns of MOB1 at Rt 7.391 and 8.935 to 31.838 min were similar to butylated hydroxytoluene (Fig. A29) and long chain saturated hydrocarbon (Fig. A30).

However, the identity of these compounds ought to be confirmed by comparing with an authentic sample.

The composition of compounds contained in MOB1 are presented in Table 4.1.15

Table 4.1.15 The compounds contained in MOB1

Rt (min)	Name
7.391	butylated hydroxytoluene
8.935 to 31.838	long chain saturated hydrocarbon

The chemical constituents of the base oil are a mixture of long chain saturated hydrocarbons. The molecular weight of the base oil in synthetic lubricants is shown in Table 4.1



Table 4.1 The molecular weight of base oils in synthetic lubricants

Synthetic Lubricant	Molecular Weight of Base Oil
Exxon	831
Shell	933
BP	707
Castrol	660
Mobil	812



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## 4.2 Structural Elucidation of Antioxidants

### Exxon

ULT2 was obtained as yellow oil. Its IR-spectrum is shown in Fig. BI. The N-H stretching vibration peak of a secondary amine compound was observed at  $3393\text{ cm}^{-1}$ . The =CH stretching vibration peak of an aromatic compound was observed at  $3028\text{ cm}^{-1}$ . The C-H stretching vibration peaks of an aliphatic compound were observed at  $2957$  and  $2855\text{ cm}^{-1}$ . The C=C stretching vibration peaks were observed at  $1599$ ,  $1500\text{ cm}^{-1}$ . The C=O stretching vibration peak was observed at  $1729\text{ cm}^{-1}$ . The absorption peaks at  $1465$  and  $1394\text{ cm}^{-1}$  correspond to C-H symmetric bending vibration mode of  $\text{CH}_3$  groups. The absorption peaks at  $823$ ,  $748$  and  $698\text{ cm}^{-1}$  correspond to =CH out of plane.

Table 4.2.1 The IR absorption band assignments of ULT2

Wavenumber ( $\text{cm}^{-1}$ )	Band type	Tentative assignment
3393	s	N-H stretching vibration of secondary amine
3028	m	C-H stretching vibration of =CH
2957,2925,2859	s	C-H stretching vibration of $-\text{CH}_3,-\text{CH}_2-$

Table 4.2.1 (Continued)

Wavenumber ( $\text{cm}^{-1}$ )	Band type	Tentative assignment
1729	s	C=O stretching vibration of ester
1599,1500	s	C=C ring stretching vibration of aromatic ring
1518	s	N-H bending vibration of secondary amine
1465,1394	m	CH bending vibration of $-\text{CH}_2-$ , $\text{CH}_3-$
1316	m	C-N stretching vibration of $-\text{CN}-$
823,748,698	m	=C-H out of plane

The  $^1\text{H}$ -NMR spectrum, Fig. B2, exhibited a signal at 3.8 ppm indicating the presence of protons attached to a carbon atom bearing an oxygen atom. This was corroborated by the presence of signals at 51.0 and 57.0 ppm in the  $^{13}\text{C}$ -NMR spectrum Fig. B3. The signals of an aromatic ring were observed around 7.3-7.5 ppm in the  $^1\text{H}$ -NMR spectrum and 117.0-129.0 ppm in the  $^{13}\text{C}$ -NMR spectrum. The  $^1\text{H}$  NMR and  $^{13}\text{C}$ -NMR are summarized in Table 4.2.2

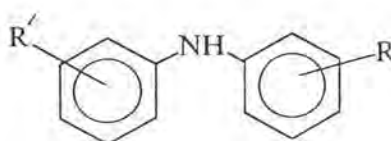


Table 4.2.2 The  $^1\text{H}$  and  $^{13}\text{C}$ -NMR chemical shifts of ULT2

$^1\text{H}$ (ppm)	$^{13}\text{C}$ (ppm)	IR ( $\text{cm}^{-1}$ )	Tentative assignment
1.0	14.5	1465, 1394	$\text{CH}_3$
1.5	23.0-38.3		$-(\text{CH}_2)_n-$
3.8	51.0,57.0	1160	O- $\text{CH}_2$
7.3-7.5	117.0-129.0	1599,1500	C=C aromatic ring

The gas chromatogram is shown in Fig. B4. The fragmentation ion patterns of ULT2 at retention time (Rt) 7.383 and 10.392 min were similar to butylated hydroxytoluene (Fig B5) and a high molecular weight ester compound (Fig. B6). The fragmentation ion patterns of ULT2 at Rt13.709 to 27.266 are shown in Fig. B7-B12. From the spectral evidence and the major structure types of aromatic amines that were shown in Table 2.3.2, a mixture of aromatic amine compound (Rt 13.709 to Rt 27.266 min) may be one of the following compounds.

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Rt 13.709 min  $R' = \text{CH}_3$ ,  $R = \text{CH}_2\text{CH}_2\text{CH}_3$  M.W. = 225

Rt 18.886 min  $R' = \text{CH}_2\text{CH}_2\text{CH}_3$ ,  $R = \text{CH}_2(\text{CH}_2)_3\text{CH}_3$  M.W. = 281

Rt 19.295 min  $R' = \text{CH}_3$ ,  $R = \text{CH}_2(\text{CH}_2)_5\text{CH}_3$  M.W. = 281

Rt 23.925 min  $R' = \text{CH}_2(\text{CH}_2)_3\text{CH}_3$ ,  $R = \text{CH}_2(\text{CH}_2)_5\text{CH}_3$ , M.W. = 337

Rt 27.266 min  $R' = \text{CH}_2(\text{CH}_2)_3\text{CH}_3$ ,  $R = \text{CH}_2(\text{CH}_2)_9\text{CH}_3$ , M.W. = 393

The compounds contained in ULT2 is presented in Table 4.2.3

Table 4.2.3 The compounds contained in ULT2

Rt (min)	Name
7.383	butylated hydroxytoluene
10.392	high molecular weight ester
13.709 to 27.266	mixture of alkylated diphenylamines

### Shell

TMO2 was obtained as red brown oil. Its IR-spectrum is shown in Fig. B13. The O-H stretching vibration peak of an alcohol compound was observed at  $3610 \text{ cm}^{-1}$ . The N-H stretching vibration peak of a secondary amine compound was observed at  $3380 \text{ cm}^{-1}$ . The =CH stretching vibration peak of

aromatic compound was observed at  $3020\text{ cm}^{-1}$ . The C-H stretching vibration peaks of an aliphatic compound were observed at  $2980$  and  $2860\text{ cm}^{-1}$ . The C=C ring stretching vibration peaks of aromatic ring were observed at  $1600$ ,  $1520\text{ cm}^{-1}$ . The C-O stretching vibration peak was observed at  $980\text{ cm}^{-1}$ .

Table 4.2.4 The IR absorption band assignments of TMO2

Wavenumber ( $\text{cm}^{-1}$ )	Band type	Tentative assignment
3610	m	O-H stretching vibration of alcohol
3380	m	N-H stretching vibration of secondary amine
3020	m	C-H stretching vibration of =CH-
2980,2860	s	C-H stretching vibration of $\text{CH}_3$ -, $\text{CH}_2$ -
1600, 1520	s	C=C ring stretching vibration of aromatic ring
1465,1394	m	CH bending vibration of $\text{-CH}_2$ -, $\text{CH}_3$ -
980	s	C-O stretching vibration of alcohol

The  $^1\text{H-NMR}$  spectrum, Fig. B14, exhibited signals at 3.9-4.1 ppm indicating the presence of protons attached to a carbon atom bearing an oxygen atom. This was corroborated by the presence of a signal at 57.5 ppm in the  $^{13}\text{C-NMR}$  spectrum (Fig. B15). The signals of an aromatic ring were observed



around 7.2-7.4 ppm in the  $^1\text{H}$ -NMR spectrum and 118.0-129.0 ppm in the  $^{13}\text{C}$ -NMR spectrum. The  $^1\text{H}$  NMR and  $^{13}\text{C}$ -NMR are summarized in Table 4.2.5

Table 4.2.5 The  $^1\text{H}$  and  $^{13}\text{C}$ -NMR chemical shifts of TMO2

$^1\text{H}$ (ppm)	$^{13}\text{C}$ (ppm)	IR ( $\text{cm}^{-1}$ )	Tentative assignment
1.0-1.95	14.0	1465, 1394	$\text{CH}_3$
1.50	23.0-38.26		$(\text{CH}_2)_n$
3.80-4.10	57.5	980	$-\text{O}-\text{CH}_2-$
7.2-7.4	118.0-129.0	1600, 1500	$\text{C}=\text{C}$ aromatic ring

The gas chromatogram is shown in Fig. B16. The fragmentation ion patterns of TMO2 at retention time (Rt) 6.925, 7.411, 20.518, 20.614, 22.107, 22.200, 22.601 and 23.291 min were similar to 2,6-bis(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione (Fig. B17), butylated hydroxytoluene (Fig B18), 1-phenyl-1-nonanol (Fig. B19), 2-n-hexylphenol (Fig. B20), 2,4-bis(dimethylbenzyl)phenol (Fig. B21), 4-(1-methylpropyl)phenol (Fig. B22), 2,4-bis(dimethylbenzyl)-6-t-butylphenyl (Fig. B23) and 2-octylphenol (Fig. B24).

However, the identity of these compounds ought to be confirmed by comparing with an authentic sample.

The fragmentation ion patterns of TMO2 at Rt13.709, 18.861, 23.911 and 27.299 min(Fig. B25-B28) were similar to the fragmentation ion patterns of ULT2 at Rt13.709, 18.886, 23.925 and 27.266 min(Fig. B7, B8, B11, B12).

The compounds contained in TMO2 is presented in Table 4.2.6.

Table 4.2.6 The compounds contained in TMO2

Rt (min)	Name
6.925	2,6-bis(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione
7.411	butylated hydroxytoluene
20.518	1-phenyl-1-nonanol
20.614	2-n-hexylphenol
22.107	2,4-bis(dimethylbenzyl)phenol
22.200	4-(1-methylpropyl)phenol
22.601	2,4-bis(dimethylbenzyl)-6-t-butylphenyl
23.291	2-octylphenol
13.709,18.861 23.911 and 27.299	mixture of alkylated diphenylamines

BP

BP2 was obtained as yellow oil. Its IR-spectrum is shown in Fig. B29. The N-H stretching vibration peak of a secondary amine compound was observed at  $3400\text{ cm}^{-1}$ . The =CH stretching vibration peak of aromatic compound was observed at  $3040\text{ cm}^{-1}$ . The C-H stretching vibration peaks of an aliphatic compound were observed at  $2980$  and  $2880\text{ cm}^{-1}$ . The C=C stretching vibration peaks of aromatic compound were observed at  $1600, 1520\text{ cm}^{-1}$ . The absorption peaks at  $1460$  and  $1380\text{ cm}^{-1}$  correspond to C-H symmetric bending vibration mode of  $\text{CH}_3$  groups. The absorption peaks at  $820, 760\text{ cm}^{-1}$  correspond to =CH out of plane.

Table 4.2.7 The IR absorption band assignments of BP2

Wavenumber ( $\text{cm}^{-1}$ )	Band type	Tentative assignment
3400	m	N-H stretching vibration of secondary amine
3040	m	C-H stretching vibration of =CH-
2980, 2880	s	C-H stretching vibration of $-\text{CH}_3-$ , $-\text{CH}_2-$
1600, 1520	s	C=C ring stretching vibration of aromatic ring
1460, 1380	s	C-H bending vibration of $-\text{CH}_2-$ , $\text{CH}_3-$
820, 760	m	=C-H out of plane



The  $^1\text{H}$ -NMR spectrum, Fig. B30, exhibited signals of an aromatic ring around 7.1-7.2 ppm in the  $^1\text{H}$ -NMR spectrum and 116.9-129.1 ppm in the  $^{13}\text{C}$ -NMR spectrum (Fig. B31). The  $^1\text{H}$  NMR and  $^{13}\text{C}$ -NMR are summarized in Table 4.2.8

Table 4.2.8 The  $^1\text{H}$  and  $^{13}\text{C}$ -NMR chemical shifts of BP2

$^1\text{H}$ (ppm)	$^{13}\text{C}$ (ppm)	IR ( $\text{cm}^{-1}$ )	Tentative assignment
0.9	14.5	1460, 1380	$\text{CH}_3$
1.4	23.0-28.0		$\sim(\text{CH}_2)_n\sim$
7.1-7.2	116.9-129.1	1600-1520	C=C aromatic

The gas chromatogram is shown in Fig. B32. The fragmentation ion patterns of BP2 at retention time (Rt) 7.397, 15.480 min were similar to butylated hydroxytoluene (Fig. B33) and 2,6-bis(t-butyl)-4-(dimethylbenzyl)phenol (Fig. B34).

However, the identity of these compounds ought to be confirmed by comparing with an authentic sample.

The components which were located at Rt 20.629 min (Fig. B35) were similar to the fragmentation ion patterns of ULT2 at Rt 19.899 min (Fig. B10)

The compounds contained in BP2 is presented in Table 4.2.9

Table 4.2.9 The compounds contained in BP2

Rt (min)	Name
7.397	butylated hydroxytoluene
15.480	2,6-bis(t-butyl)-4-(dimethylbenzyl)phenol
20.629	alkylated diphenylamine

### Castrol

CAS2 was obtained as yellow oil. Its IR-spectrum is shown in Fig. B36. The N-H stretching vibration peak of a secondary amine compound was observed at  $3400\text{ cm}^{-1}$ . The C-H stretching vibration peaks of an aliphatic compound were observed at  $2980$ ,  $2940$  and  $2880\text{ cm}^{-1}$ . The C=O stretching vibration peak of an ester compound was observed at  $1740\text{ cm}^{-1}$ . The C=C stretching vibration peaks of aromatic compound were observed at  $1600$ ,  $1520\text{ cm}^{-1}$ . The absorption peaks at  $1460$  and  $1380\text{ cm}^{-1}$  correspond to C-H symmetric bending vibration mode of  $\text{CH}_3$  groups. The C-O stretching vibration peaks of an ester compound were observed at  $1180$  and  $980\text{ cm}^{-1}$ .

Table 4.2.10 The IR absorption band assignments of CAS2

Wavenumber ( $\text{cm}^{-1}$ )	Band type	Tentative assignment
3400	m	N-H stretching vibration of secondary amine
2980, 2940, 2880	s	C-H stretching vibration of $-\text{CH}_3, -\text{CH}_2$
1740	s	C=O stretching vibration of ester
1600, 1520	s	C=C ring stretching vibration of aromatic ring
1460, 1380	s	C-H bending vibration of $-\text{CH}_2-, -\text{CH}_3$
1180, 980	s,b	C-O stretching

The  $^1\text{H}$ -NMR spectrum, Fig. B37, exhibited a signal at 3.9 ppm indicating the presence of protons attached to a carbon atom bearing an oxygen atom. This was corroborated by the presence of signals at 62.3-64.5 ppm in the  $^{13}\text{C}$ -NMR spectrum (Fig. B38). The signals of an aromatic ring were observed around 6.9-7.1 ppm in the  $^1\text{H}$ -NMR spectrum and 117.3-129.0 ppm in the  $^{13}\text{C}$ -NMR spectrum. The signal at 173.3 ppm belonged to a carbon of the carboxylic part of ester molecule.

The  $^1\text{H}$  NMR and  $^{13}\text{C}$ -NMR are summarized in Table 4.2.11



Table 4.2.11 The  $^1\text{H}$  and  $^{13}\text{C}$ -NMR chemical shifts of CAS2

$^1\text{H}$ (ppm)	$^{13}\text{C}$ (ppm)	IR ( $\text{cm}^{-1}$ )	Tentative assignment
0.8	14.0	1460, 1380	$-\text{CH}_3$
1.1	22.3-34.1		$-(\text{CH}_2)_n-$
3.9	62.3-64.5	1180, 980	$\text{O}-\text{CH}_2$
6.9-7.1	117.3-129.0	1600, 1520	$\text{C}=\text{C}$ aromatic ring
	173.3	1740	$\text{CO}_2\text{R}$

The gas chromatogram is shown in Fig. B39. The fragmentation ion patterns of CAS2 at retention time (Rt) 7.404, 14.787, 15.485, 16.163 and 22.095 min were similar to butylated hydroxytoluene (Fig. B40), 2-t-butyl-4-(dimethylbenzyl)phenol (Fig. B41), 2,6-bis(t-butyl)-4-(dimethylbenzyl)phenol (Fig. B42), methyl-(9Z)-octadecenoate (Fig. B43) and 2,4-bis(dimethylbenzyl)phenol (Fig. B44).

The components which were located at Rt 13.723 (Fig. B45) and 18.827 min (Fig. B46) were similar to the fragmentation ion patterns of ULT2 at Rt 13.709 (Fig. B7) and 18.866 min (Fig. B8).

However, the identity of these compounds ought to be confirmed by comparing with an authentic sample.

The compounds contained in CAS2 is presented in Table 4.2.12

Table 4.2.12 The compounds contained in CAS2

Rt (min)	Name
7.404	butylated hydroxytoluene
13.723	alkylated diphenylamine
14.787	2-t-butyl-4-(dimethylbenzyl)phenol
15.485	2,6-bis(t-butyl)-4-(dimethylbenzyl)phenol
16.163	methyl-(9Z)-octadecenoate
18.827	alkylated diphenylamine
22.095	2,4-bis(dimethylbenzyl)phenol

### Mobil

MOB2 was obtained as yellow oil. Its IR-spectrum is shown in Fig. B47. The OH stretching was observed at  $3640\text{ cm}^{-1}$ . The C-H stretching vibration peaks of an aliphatic compound were observed at  $2980$ ,  $2940$  and  $2880\text{ cm}^{-1}$ . The C=O stretching vibration peak of an ester compound was observed at  $1730\text{ cm}^{-1}$ . The absorption peaks at  $1460$ ,  $1380\text{ cm}^{-1}$  correspond to C-H symmetric bending vibration mode of  $\text{CH}_3$  groups. The C-O stretching vibration peaks of an ester compound were observed at  $1200$  and  $980\text{ cm}^{-1}$ .

Table 4.2.13 The IR absorption band assignments of MOB2

Wavenumber ( $\text{cm}^{-1}$ )	Band type	Tentative assignment
3640	m	O-H stretching vibration
2980, 2940, 2880	s	C-H stretching of $-\text{CH}_3, -\text{CH}_2-$
1730	s	C=O stretching vibration of ester
1460, 1380	m	C-H bending vibration of $-\text{CH}_2-, \text{CH}_3-$
1200, 980	s, b	C-O stretching vibration of ester

The  $^1\text{H}$ -NMR spectrum, Fig. B48, exhibited a signal at 4.1 ppm indicating the presence of protons attached to a carbon atom bearing an oxygen atom. This was corroborated by the presence of signals at 62.7 to 64.8 ppm in the  $^{13}\text{C}$ -NMR spectrum (Fig. B49). The signals of an aromatic ring were observed around 6.9-7.1 ppm in the  $^1\text{H}$ -NMR spectrum and 124.7-135.3 and 152.7 ppm in the  $^{13}\text{C}$ -NMR spectrum. The signal at 171.7 ppm belonged to a carbonyl carbon. The  $^1\text{H}$  NMR and  $^{13}\text{C}$ -NMR are summarized in Table 4.2.14.



Table 4.2.14 The  $^1\text{H}$  and  $^{13}\text{C}$ -NMR chemical shifts of MOB2

$^1\text{H}$ (ppm)	$^{13}\text{C}$ (ppm)	IR ( $\text{cm}^{-1}$ )	Tentative assignment
0.8	14.0	1460-1380	$-\text{CH}_3$
1.3	21.7-47.3		$-(\text{CH}_2)_n-$
4.1	62.7-64.8	1200, 980	$-\text{O}-\text{CH}_2$
6.9-7.1	124.7-135.3, 152.7		$\text{C}=\text{C}$ aromatic ring

The gas chromatogram displayed peaks at retention times (Rt) 7.377, 24.327, 29.753 min (Fig. B50). The fragmentation ion patterns of MOB2 at retention time (Rt) 7.377, 24.327, 29.753 min were similar to butylated hydroxytoluene (Fig. B51), bis(3,5-di-tert-butyl-4-hydroxyphenyl)methane (Fig. B52) and didecyl decanedioate (Fig. B53).

However, the identity of these compounds ought to be confirmed by comparing with an authentic sample. The compounds contained in MOB2 are presented in Table 4.2.15.

Table 4.2.15 The compounds contained in MOB2

Rt (min)	Name
7.377	butylated hydroxytoluene
24.327	bis(3,5-di-tert-butyl-4-hydroxyphenyl)methane
29.753	didecyl decanedioate



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#### 4.3 Structural Elucidations of Antiwear and Dispersant agents

##### Exxon

##### ULT3

ULT3 was obtained as yellowish green oil. Its IR-spectrum is shown in Fig. C1. The C=O overtone was observed at  $3473\text{ cm}^{-1}$ . The C-H stretching vibrations peaks of an aliphatic compound were observed at 2955, 2926 and  $2856\text{ cm}^{-1}$ . The C=O stretching vibrations peak of an ester was observed at  $1743\text{ cm}^{-1}$ . The absorptions peaks at 1466 and  $1384\text{ cm}^{-1}$  correspond to C-H symmetric bending vibrations mode of  $\text{CH}_3$  groups. The C-O stretching vibrations peak of an ester was observed at  $1158\text{ cm}^{-1}$ .

Table 4.3.1 The IR absorptions band assignments of ULT3

Wavenumber ( $\text{cm}^{-1}$ )	Band type	Tentative assignment
3473-3387	w	C=O overtone
2955,2926,2856	s	C-H stretching vibrations of $-\text{CH}_3,-\text{CH}_2-$
1743	s	C=O stretching vibrations of ester
1600	m	C=C ring stretching vibrations of aromatic ring
1466,1384	m	C-H bending vibrations of $-\text{CH}_2-, \text{CH}_3-$



Table 4.3.1 (Continued)

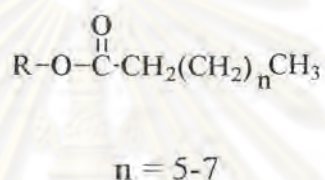
Wavenumber ( $\text{cm}^{-1}$ )	Band type	Tentative assignment
1158	s,b	C-O stretching vibrations of ester
783,749,725	m	C-H rocking mode of $\text{CH}_2$

The  $^1\text{H}$ -NMR Spectrum, Fig. C2, exhibited a signal at 3.8 ppm indicating the presence of protons attached to a carbon atom bearing a oxygen atom. This was corroborated by the presence of a signal at 63 ppm in the  $^{13}\text{C}$ -NMR Spectrum.(Fig. C3).The signal at 173.8 ppm belonged to a carbonyl carbon of ester. The spectral data are summarized in Table 4.3.2

Table 4.3.2 The  $^1\text{H}$  and  $^{13}\text{C}$ -NMR chemical shifts of ULT3

$^1\text{H}$ (ppm)	$^{13}\text{C}$ (ppm)	IR ( $\text{cm}^{-1}$ )	Tentative assignment
0.7	14.0	1466, 1384	$\text{CH}_3$
1.0	23.0-33.0		$-(\text{CH}_2)_n-$
3.7	63..0		$-\text{OCH}_2$
	173.8	1740, 1160	$-\text{CO}_2\text{R}$

The gas chromatogram is shown in Fig. C4. The fragmentation ions patterns of ULT3 at retention time (Rt) 29.421, 30.949 and 32.354 min are shown in Fig. C5-C7. From the spectral evidence, ULT3 were a mixture of high molecular weight esters. ULT3 may be one or more of the following compounds.



#### ULT4

ULT4 was obtained as red-brown oil. Its IR-spectrum is shown in Fig. C8. The OH stretching was observed at  $3479\text{ cm}^{-1}$ . The C-H stretching vibrations peaks of an aliphatic compound were observed at 2957, 2929 and  $2857\text{ cm}^{-1}$ . The C=O stretching vibrations peak of an ester was observed at  $1743\text{ cm}^{-1}$ . The absorptions peaks at 1466 and  $1384\text{ cm}^{-1}$  correspond to C-H symmetric bending vibrations mode of  $\text{CH}_3$  groups. The C-O stretching vibrations peak of an ester was observed at  $1160\text{ cm}^{-1}$ .

Table 4.3.3 The IR absorptions band assignments of ULT4

Wavenumber ( $\text{cm}^{-1}$ )	Band type	Tentative assignment
3479	w	O-H stretching vibrations of alcohol
2957,2929,2857	s	C-H stretching vibrations of $-\text{CH}_3$ , $-\text{CH}_2-$
1743	s	C=O stretching vibrations of ester
1600	m	C=C ring stretching vibrations of aromatic ring
1466,1384	m	C-H bending vibrations of $-\text{CH}_2-$ , $-\text{CH}_3$
1160	s,b	C-O stretching vibrations of ester

The  $^1\text{H-NMR}$  Spectrum, Fig. C9, exhibited a signal at 3.8 ppm indicating the presence of protons attached to a carbon atom bearing a oxygen atom. This was corroborated by the presence of a signal at 63.0 ppm in the  $^{13}\text{C-NMR}$  Spectrum (Fig. C10). The signal at 173.8 ppm belonged to a carbonyl carbon of ester. The spectral data are summarized in Table 4.3.4



Table 4.3.4 The  $^1\text{H}$  and  $^{13}\text{C}$ -NMR chemical shifts of ULT4

$^1\text{H}$ (ppm)	$^{13}\text{C}$ (ppm)	IR ( $\text{cm}^{-1}$ )	Tentative assignment
0.7	14.0	1466, 1384	$\text{CH}_3$
1.0	23.0-33.0		$-(\text{CH}_2)_n-$
3.7	63.0		$-\text{OCH}_2$
	173.8	1740, 1160	$-\text{CO}_2\text{R}$

The gas chromatogram is shown in Fig. C11. The fragmentation ions patterns of ULT4 at retention time (Rt) 4.750, 6.275, 7.399 and 10.231 min were similar to octanoic acid (Fig. C12), decanoic acid (Fig. C13), butylated hydroxytoluene (Fig. C14) and 4-(2,2,3,3-tetramethylbutyl)phenol (Fig. C15).

However, the identity of these compounds ought to be confirmed by comparing with an authentic sample.

The fragmentation ions patterns of ULT4 at Rt 23.872, 26.043, 29.373, 30.888 and 32.339 min (Fig. C16-C20) were similar to the fragmentation ions patterns of ULT3 at Rt 29.421, 30.949 and 32.354 min (Fig. B7-B12).

The compounds contained in ULT4 are presented in Table 4.3.5

Table 4.3.5 The compounds contained in ULT4

Rt (min)	Name
4.750	octanoic acid
6.275	decanoic acid
7.399	butylated hydroxytoluene
10.231	4-(2,2,3,3-tetramethylbutyl)phenol
23.872	long chain ester compound
26.043	long chain ester compound
29.373	long chain ester compound
30.888	long chain ester compound
32.339	long chain ester compound

### Shell

#### TMO3

TMO3 was obtained as yellow oil. Its IR-spectrum is shown in Fig. C21. The C=O overtone was observed at  $3460\text{ cm}^{-1}$ . The C-H stretching vibrations peaks of an aliphatic compound were observed at 2960, 2920 and  $2860\text{ cm}^{-1}$ . The C=O stretching vibrations peak of an ester was observed at  $1740.\text{cm}^{-1}$ . The absorptions peaks at 1470 and  $1380\text{ cm}^{-1}$  correspond to C-H symmetric bending vibrations mode of  $\text{CH}_3$  groups. The C-O stretching vibrations peak of an ester was observed at  $1160\text{ cm}^{-1}$ .

Table 4.3.6 The IR absorptions band assignments of TMO3

Wavenumber ( $\text{cm}^{-1}$ )	Band type	Tentative assignment
3460	w	C=O overtone
2960, 2920, 2860	s	C-H stretching vibrations of $-\text{CH}_3, -\text{CH}_2-$
1740	s	C=O stretching vibrations of ester
1470, 1380	m	C-H bending vibrations of $-\text{CH}_2-, -\text{CH}_3$
1160, 980	s,b	C-O stretching vibrations of ester

The  $^1\text{H-NMR}$  Spectrum, Fig.C22 , exhibited a signal at 3.9 ppm indicating the presence of protons attached to a carbon atom bearing a oxygen atom. This was corroborated by the presence of a signal at 63.5 ppm in the  $^{13}\text{C-NMR}$  Spectrum.(Fig.C23). The signal at 173.0 ppm belonged to a carbonyl carbon. The spectral data are summarized in Table 4.3.7.

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Table 4.3.7 The  $^1\text{H}$  and  $^{13}\text{C}$ -NMR chemical shifts of TMO3

$^1\text{H}$ (ppm)	$^{13}\text{C}$ (ppm)	IR ( $\text{cm}^{-1}$ )	Tentative assignment
0.80	13.5	1465, 1394	$\text{CH}_3$
1.0-2.2	22.0-34.0		$(\text{CH}_2)_n$
3.90	63.5	1160	$-\text{OCH}_2$
	173.0	1740-1160	$-\text{CO}_2\text{R}$

The gas chromatogram is shown in Fig. C24. The fragmentation ions patterns of TMO3 at retention time (Rt) 29.414, 30.928 and 32.329 min (Fig. C25-C27) were similar to the fragmentation ions patterns of ULT3 at Rt 29.421, 30.949 and 32.354 min (Fig. C5, C6, C7). From the spectral evidence, TMO3 was a mixture of long chain esters.

BP

BP3

BP3 was obtained as yellow oil. Its IR-spectrum is shown in Fig. C28. The C=O overtone was observed at  $3400\text{ cm}^{-1}$ . The C-H stretching vibrations peaks of an aliphatic compound were observed at  $2980$  and  $2860\text{ cm}^{-1}$ . The C=O stretching vibrations peak was observed at  $1720\text{ cm}^{-1}$ . The C=C ring stretching vibrations of an aromatic ring was observed at  $1600\text{ cm}^{-1}$ . The absorptions peaks at  $1460$  and  $1380\text{ cm}^{-1}$  correspond to C-H

symmetric bending vibrations mode of  $\text{CH}_3$  groups. The C-O stretching vibrations peaks of an ester were observed at 1173 and 980  $\text{cm}^{-1}$ .

Table 4.3.8 The IR absorptions band assignments of BP3

Wavenumber ( $\text{cm}^{-1}$ )	Band type	Tentative assignment
3400	w	C=O overtone
2980, 2860	s	C-H stretching vibrations of $-\text{CH}_3-$ , $-\text{CH}_2-$
1720	s	C=O stretching vibrations of ester
1600	m	C=C ring stretching vibrations of aromatic ring
1460, 1380	m	C-H bending vibrations of $-\text{CH}_2-$ , $\text{CH}_3-$
1290, 980	s,b	C-O stretching vibrations of ester

The  $^1\text{H}$ -NMR spectrum, Fig. C29, exhibited a signal at 3.7 ppm indicating the presence of protons attached to a carbon atom bearing an oxygen atom. This was corroborated by the presence of a signal at 64.2 ppm in the  $^{13}\text{C}$ -NMR spectrum (Fig. C30). The signals of an aromatic ring were observed around 6.7-8.0 ppm in  $^1\text{H}$ -NMR spectrum and 117.6-127.3 ppm in the  $^{13}\text{C}$ -NMR spectrum. The  $^1\text{H}$  NMR and  $^{13}\text{C}$ -NMR are summarized in Table 4.3.9

Table 4.3.9 The  $^1\text{H}$  and  $^{13}\text{C}$ -NMR chemical shifts of BP3

$^1\text{H}$ (ppm)	$^{13}\text{C}$ (ppm)	IR ( $\text{cm}^{-1}$ )	Tentative assignment
0.8	14.0		$\text{CH}_3$
1.2	19.1-48.6		$-(\text{CH}_2)_n-$
3.7	47.0-65.0	1170,980	$-\text{OCH}_2$
6.7	114.5-133.0	1600	$\text{C}=\text{C}$ aromatic

The gas chromatogram is shown in Fig. C31. The fragmentation ions patterns of BP3 at retentions time (Rt) 7.400, 9.978, 13.821, 16.292 and 23.110 min were similar to butylated hydroxytoluene (Fig. C32), trichloroheptafluorobutane (Fig. C33), 4-dodecylphenol (Fig. C34), methyl-(9E)-dodecenoate (Fig. C35), and diisooctyl phthalate (Fig. C36).

However, the identity of these compounds ought to be confirmed by comparing with an authentic sample

The compounds contained in BP3 are presented in Table 4.3.10



Table 4.3.10 The compounds contained in BP3

Rt (min)	Name
7.400	butylated hydroxytoluene
9.978	trichloroheptafluorobutane
13.821	4-dodecylphenol
16.292	methyl-(9E)-dodecenoate
23.110	diisooctyl phthalate

#### BP4

BP4 was obtained as blue oil. Its IR-spectrum is shown in Fig. C37. The C=O overtone was observed at  $3420\text{ cm}^{-1}$ . The C-H stretching vibrations peaks of an aliphatic compound were observed at  $2960$  and  $2860\text{ cm}^{-1}$ . The C=O stretching vibrations peak of an ester was observed at  $1730\text{ cm}^{-1}$ . The absorptions peaks at  $1460$  and  $1380\text{ cm}^{-1}$  correspond to C-H symmetric bending vibrations mode of  $\text{CH}_3$  groups. The C-O stretching vibrations peaks of an were observed at  $1180$  and  $980\text{ cm}^{-1}$ .

Table 4.3.11 The IR absorptions band assignments of BP4

Wavenumber ( $\text{cm}^{-1}$ )	Band type	Tentative assignment
3420	w	C=O overtone
2960, 2860	s	C-H stretching vibrations of $-\text{CH}_3, -\text{CH}_2-$
1730	s	C=O stretching vibrations of ester
1460, 1380	m	C-H bending vibrations of $-\text{CH}_2-, -\text{CH}_3$
1180, 980	s,b	C-O stretching vibrations of ester

The  $^1\text{H-NMR}$  Spectrum, Fig. C38 , exhibited a signal at 4.0 ppm indicating the presence of protons attached to a carbon atom bearing a oxygen atom. This was corroborated by the presence of a signal at 64.6 ppm in the  $^{13}\text{C-NMR}$  Spectrum (Fig. C39). The signal at 176.4 ppm belongs to a carbonyl carbon of an ester. The spectral data are summarized in Table 4.3.12

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Table 4.3.12 The  $^1\text{H}$  and  $^{13}\text{C}$ -NMR chemical shifts of BP4

$^1\text{H}$ (ppm)	$^{13}\text{C}$ (ppm)	IR ( $\text{cm}^{-1}$ )	Tentative assignment
0.9	14.0	1460, 1380	$-\text{CH}_3$
1.3	19.0-30.5		$-(\text{CH}_2)_n-$
4.0	64.6		$-\text{OCH}_2$
	176.4	1740	$-\text{CO}_2\text{R}$

The gas chromatogram is shown in Fig. C40. The fragmentation ions patterns of BP4 at 7.417 and 14.120 min were similar to butylated hydroxytoluene (Fig. C41) and dodecylphenol (Fig. C42)

However, the identity of these compounds ought to be confirmed by comparing with an authentic sample

The compounds contained in BP4 are presented in Table 4.3.13

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Table 4.3.13 The compounds contained in BP4

Rt (min)	Name
7.417	butylated hydroxytoluene
14.120	dodecylphenol

CastrolCAS3

CAS3 was obtained as yellow oil. Its IR-spectrum is shown in Fig. C43. The O-H stretching vibrations peak was observed at  $3400\text{ cm}^{-1}$ . The C-H stretching vibrations peaks of an aliphatic compound were observed at  $2980$ ,  $2940$  and  $2880\text{ cm}^{-1}$ . The C=O stretching vibrations peak of an ester was observed at  $1750\text{ cm}^{-1}$ . The C=C stretching vibrations peaks of aromatic compound were observed at  $1600$  and  $1520\text{ cm}^{-1}$ . The absorptions peaks at  $1475$  and  $1390\text{ cm}^{-1}$  correspond to C-H symmetric bending vibrations mode of  $\text{CH}_3$  groups. The C-O stretching vibrations peaks of an ester were observed at  $1180$  and  $980\text{ cm}^{-1}$ .

Table 4.3.14 The IR absorptions band assignments of CAS3

Wavenumber ( $\text{cm}^{-1}$ )	Band type	Tentative assignment
3400	m	O-H stretching
2980, 2940, 2880	s	C-H stretching vibrations of $-\text{CH}_3, -\text{CH}_2-$
1750	s	C=O stretching vibrations of ester
1600, 1520	s	C=C ring stretching vibrations of aromatic ring
1475, 1390	s	C-H bending vibrations of $-\text{CH}_2-, -\text{CH}_3$
1180, 980	s,b	C-O stretching vibrations of ester

The  $^1\text{H}$ -NMR spectrum, Fig. C44, exhibited a signal at 4.0 ppm indicating the presence of protons attached to a carbon atom bearing an oxygen atom. This was corroborated by the presence of signals at 63.1-65.0 ppm in the  $^{13}\text{C}$ -NMR spectrum (Fig. C45). The signals of an aromatic ring were observed around 6.2-7.1 ppm in  $^1\text{H}$ -NMR spectrum and 114.6-128.3 ppm in the  $^{13}\text{C}$ -NMR spectrum. The signal at 174.3 ppm belonged to a carbonyl carbon of ester. The  $^1\text{H}$  NMR and  $^{13}\text{C}$ -NMR spectra are summarized in Table 4.3.15

Table 4.3.15 The  $^1\text{H}$  and  $^{13}\text{C}$ -NMR chemical shifts of CAS3

$^1\text{H}$ (ppm)	$^{13}\text{C}$ (ppm)	IR ( $\text{cm}^{-1}$ )	Tentative assignment
0.8	14.1	1475, 1390	$\text{CH}_3$
1.1-2.2	22.1-34.3		$-(\text{CH}_2)_n$
4.0	63.1-65.0	1180, 980	O- $\text{CH}_2$
6.2-7.1	114.6-128.3	1600, 1520	C=C aromatic ring
	174.3	1750	$\text{CO}_2\text{R}$

The gas chromatogram is shown in Fig. C46. The fragmentation ions patterns of CAS3 at retention time (Rt) 7.388 and 13.768 min were similar to butylated hydroxytoluene (Fig. C47) and dodecylphenol (Fig. C48). However, the identity of these compounds ought to be confirmed by comparing with an authentic sample. The compounds contained in CAS3 are presented in Table 4.3.16

Table 4.3.16 The compounds contained in CAS3

Rt (min)	Name
7.388	butylated hydroxytoluene
13.768	dodecylphenol



### CAS4

CAS4 was obtained as blue oil. Its IR-spectrum is shown in Fig. C49. The O-H stretching vibrations peak was observed at  $3640\text{ cm}^{-1}$ . The C-H stretching vibrations peaks of an aliphatic compound were observed at 2960, 2920 and  $2860\text{ cm}^{-1}$ . The C=O stretching vibrations peak of an ester was observed at  $1740\text{ cm}^{-1}$ . The C=C stretching vibrations peaks of aromatic compound were observed at 1610 and  $1510\text{ cm}^{-1}$ . The absorptions peaks at 1430 and  $1380\text{ cm}^{-1}$  correspond to C-H symmetric bending vibrations mode of  $\text{CH}_3$  groups. The C-O stretching vibrations peaks of an ester were observed at 980,  $1160\text{ cm}^{-1}$ .

Table 4.3.17 The IR absorptions band assignments of CAS4

Wavenumber ( $\text{cm}^{-1}$ )	Band type	Tentative assignment
3640	m	O-H stretching
2960, 2920, 2860	s	C-H stretching vibrations of $-\text{CH}_3, -\text{CH}_2-$
1740	s	C=O stretching vibrations of ester
1610, 1510	s	C=C ring stretching vibrations of aromatic ring
1430, 1380	s	C-H bending vibrations of $-\text{CH}_2-, \text{CH}_3-$
1160, 980	s,b	C-O stretching vibrations of ester

The  $^1\text{H}$ -NMR Spectrum, Fig. C50., exhibited signals at 3.7-4.2 ppm indicating the presence of protons attached to a carbon atom bearing a oxygen atom. This was corroborated by the presence of a signal at 63.6 ppm in the  $^{13}\text{C}$ -NMR Spectrum.(Fig. C51). The signals of an aromatic ring were observed around 5.1-7.0 ppm in  $^1\text{H}$ -NMR spectrum and 124.6-152.6 ppm in the  $^{13}\text{C}$ -NMR spectrum. The signal at 173.3 ppm belonged to a carbonyl carbon of an ester. The spectral data are summarized in Table 4.3.18.

Table 4.3.18 The  $^1\text{H}$  and  $^{13}\text{C}$ -NMR chemical shifts of CAS4

$^1\text{H}$ (ppm)	$^{13}\text{C}$ (ppm)	IR ( $\text{cm}^{-1}$ )	Tentative assignment
0.9	14.0	1430, 1380	$-\text{CH}_3$
1.3	30.0-36.7		$-(\text{CH}_2)_n-$
3.7-4.2	63.6	1160, 980	$-\text{OCH}_2-$
5.1-7.0	124.6-152.5	1610, 1510	$\text{C}=\text{C}$ aromatic
	173.3	1740	$-\text{CO}_2\text{R}$

The gas chromatogram is shown in Fig. C52. The fragmentation ions patterns of CAS2 at retentions time (Rt) 6.768, 7.417, 10.022, 14.131, 16.016, 21.297 and 26.891 min were similar to tridecanol (Fig. C53), butylated hydroxytoluene (Fig. C54), 1-tetracosanol (Fig. C55), dodecylphenol (Fig.

C56), 1-nonadecanol (Fig. C57), mono(2-ethylhexyl)hexanedioate (Fig. C58) and heptanoic anhydride (Fig. C59)

However, the identity of these compounds ought to be confirmed by comparing with an authentic sample

The compounds contained in CAS4 are presented in Table 4.3.19

Table 4.3.19 The compounds contained in CAS4

Rt (min)	Name
6.768	tridecanol
7.417	butylated hydroxytoluene
10.022	1-tetracosanol
14.131	dodecylphenol
16.016	1-nonadecanol
21.297	mono(2-ethylhexyl)hexanedioate
26.891	heptanoic acid, anhydride

Mobil

MOB3

MOB3 was obtained as brown oil. Its IR-spectrum is shown in Fig. C60. The hydrogen bonded was observed at  $3400\text{ cm}^{-1}$ . The C-H stretching vibrations peaks of an aliphatic compound were observed at 2980 and



2880  $\text{cm}^{-1}$ . The C=O stretching vibrations peak of an ester was observed at 1740  $\text{cm}^{-1}$ . The absorptions peaks at 1470, 1380  $\text{cm}^{-1}$  correspond to C-H symmetric bending vibrations mode of  $\text{CH}_3$  groups. The C-O stretching vibrations peaks of an ester were observed at 1180 and 980  $\text{cm}^{-1}$ .

Table 4.3.20 The IR absorptions band assignments of MOB3

Wavenumber ( $\text{cm}^{-1}$ )	Band type	Tentative assignment
3400	w	C=O overtone
2980, 2880	s	C-H stretching vibrations of $-\text{CH}_3, -\text{CH}_2-$
1740	s	C=O stretching vibrations of ester
1470, 1380	m	C-H bending vibrations of $-\text{CH}_2-, -\text{CH}_3$
1180, 980	s,b	C-O stretching vibrations of ester

The  $^1\text{H-NMR}$  Spectrum, Fig. C61, exhibited signals at 3.6-4.7 ppm indicating the presence of protons attached to a carbon atom bearing a oxygen atom. This was corroborated by the presence of signals at 62.3-73.1 ppm in the  $^{13}\text{C-NMR}$  Spectrum.(Fig. C62).The signal at 177.1 ppm belonged to a carbonyl carbon of an ester. The spectral data are summarized in Table 4.3.21

Table 4.3.21 The  $^1\text{H}$  and  $^{13}\text{C}$ -NMR chemical shifts of MOB3

$^1\text{H}$ (ppm)	$^{13}\text{C}$ (ppm)	IR ( $\text{cm}^{-1}$ )	Tentative assignment
0.7	14.0	1470, 1380	$-\text{CH}_3$
1.1	23.0-33.0		$-(\text{CH}_2)_n-$
3.6-4.7	62.3-73.1	1180, 980	$-\text{OCH}_2$
	177.1	1740	$-\text{CO}_2\text{R}$

The gas chromatogram is shown in Fig. C63. The fragmentation ions patterns of MOB3 at Rt 6.226, 6.731, 7.388, 10.475 and 23.063 min were similar to tridecanol (Fig. C64), dioctadecyl phosphonate (Fig. C65), butylated hydroxytoluene (Fig. C66) 4,5-dihydro-1,4,5-trimethyl-1h-tetrazaborole (Fig. C67) and diisooctyl phthate (Fig. 68).

The compounds contained in MOB3 are presented in Table 4.3.22

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Table 4.3.22 The compounds contained in MOB3

Rt (min)	Name
6.226	tridecanol
6.731	dioctadecyl phosphonate
7.388	butylated hydroxytoluene
10.475	4,5-dihydro-1,4,5-trimethyl-1h-tetrazaborole
23,063	diisooctyl phthalate



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