Supporting Information For

The first iron-catalysed aluminium-variant Negishi coupling: critical effect of co-existing salts on the dynamic equilibrium of the arylaluminium species and their catalytic activity

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General. All the reactions dealing with air- or moisture-sensitive compounds were carried out in a dry reaction vessel under the positive pressure of argon gas. The air- and moisture-sensitive liquids and solutions were transferred via a syringe or a stainless steel cannula. Analytical thin-layer chromatography (TLC) was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator (Merck, #1.05715.0009). The TLC plates were visualized by exposure to ultraviolet light (254 nm) and/or by immersion in an acidic staining solution of *p*-anisaldehyde, followed by heating on a hot plate. The organic solutions were concentrated using rotary evaporation at *ca*. 30 mmHg. Flash column chromatography was performed on Kanto silica gel 60 (spherical, neutral, 140–325 mesh), as described by Still *et al.*[1]

Instrumentation. The proton nuclear magnetic resonance (^{1}H NMR), carbon NMR (^{13}C NMR), and aluminium NMR (^{27}Al NMR) spectra were recorded on a JEOL EX-270 (270 MHz) or Varian Mercury VX (300 MHz) NMR spectrometer. The proton chemical shift values are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane, and are referenced to the residual proton signal of $CDCl_3$ (δ 7.26). The ^{13}C NMR spectra were recorded at 67.8 or 75.5 MHz. The chemical shifts of the carbon atoms are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane, and are referenced to the carbon resonance of $CDCl_3$ (δ 77.36). The ^{27}Al NMR spectra were recorded at 78.2 MHz. The chemical shift of the aluminium is reported in parts per million (ppm, δ scale) and is referenced to the aluminium resonance of a 1.0 M D_2O solution of aluminium nitrate nonahydrate as an external standard. The data are presented as: chemical shift,

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(1) W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* 1978, **43**, 2923–2925.

multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, m = multiplet and/or multiplet resonances, and br = broad), coupling constant in hertz (Hz), signal area integration in natural numbers, and assignment (in *italics*).

Solvent. The anhydrous tetrahydrofuran (THF) used was purchased from the Wako Chemical Co. and distilled from benzophenone ketyl under argon (at atmospheric pressure) immediately before use. The water content of the solvent was determined using a Karl-Fischer moisture titrator (MKC-210, Kyoto Electronics Company) and found to be < 15 ppm.

Materials. The chemical reagents used were purchased from Wako Pure Chemical Industries, Ltd (Wako), Tokyo Chemical Industry Co. Ltd, Aldrich Inc., and other commercial suppliers. The Florisil® (100–200 mesh) used was purchased from Nacalai Tesque Inc. The anhydrous $FeCl_3$ (powder, 99.99%) used was purchased from Aldrich Inc., and dissolved in THF at 0 °C prior to use. Anhydrous $AlCl_3$ (powder, 99.999%) was purchased from Aldrich Inc. The arylmagnesium bromides (ArMgBr) used were prepared from the corresponding aryl bromides and magnesium turnings using a standard method, and titrated before use. All the arylmagnesium chlorides were prepared from the corresponding arylchlorides and magnesium turnings activated by washing with $CHCl_3$.

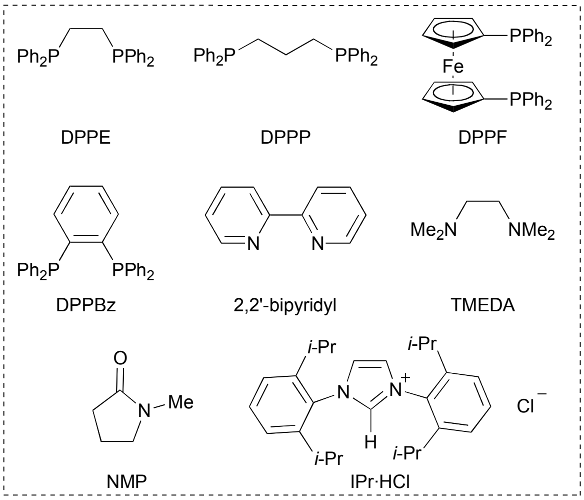
GC analysis. The yield (using undecane as an internal standard) was determined for the crude product using GC analysis on a Shimadzu GC-17A analyser equipped with an FID detector and a capillary column, HR-1 (Shinwa, 25 m × 0.25 mm i.d., film thickness = 0.25 μm).

Screening of the additives and arylmetal reagents (Table 1 with additional data (Table S1))

The arylmetal reagents in THF or Bu_2O (1.80 mmol) were added to a solution of $AlCl_3$ (80.0 mg, 0.60 mmol) in 0.6 mL of THF at 0 °C. The reaction mixture was stirred at room temperature for 1 h, and then cooled to 0 °C. To the resulting solution were added the ligand, a THF solution of $FeCl_3$ (0.15 mL, 0.015 mmol) and haloalkane (0.5 mmol), in that order. The coupling reaction was carried out at 80 °C for 3–24 h. After cooling the mixture to ambient temperature, an aliquot of the reaction mixture was taken to determine the yield of the products by GC analysis using undecane as an internal standard.

Table S1. Cross-coupling between bromocycloheptane **2** and phenylaluminium prepared from PhMgCl in the presence of various additives and ligands.

entry^a	additive (mol%)	yield (%)^{b,c}			recovery 3 (%)^{b,c}
		4	5	6	
1	none (–)	72	8	16	0
2	PPh_3 (12)	70	6	9	16
3	PCy_3 (12)	52	6	10	30
4	DPPE (6)	87	2	5	5
5	DPPP (6)	76	2	5	16
6	DPPF (6)	60	4	11	23
7	DPPBz (6)	94	<1	4	0
8	DPPBz (3)	94	<1	6	<1
9	$FeCl_2(dppbz)_2$^{d} (3)	93	0	7	0
10	2,2'-bipyridyl (6)	87	2	5	0
11	TMEDA (500)	68	1	2	29
12	NMP (500)	39	2	13	42
13	IPr·HCl (6)	66	6	8	19

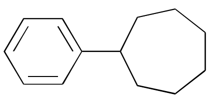


^{a}Reactions were carried out on the 0.5 mmol scale. ^{b}Reaction time was 24 h for all entries. ^{c}The yield was determined by GLC analysis by using undecane as an internal standard. ^{d}$FeCl_2(dppbz)_2$ (3 mol%) was used instead of $FeCl_3$ and an additive.

A typical procedure for the preparation of the samples for the ^{27}Al NMR experiments

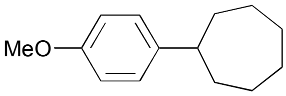
The phenylmetal reagent in THF or Bu_2O (1.80 mmol) was added to a solution of $AlCl_3$ (40.0 mg, 0.30 mmol) in 0.3 mL of THF-d_8 at 0 °C. Additional THF-d_8 was added to adjust the concentration of the reaction mixture to 0.28 M. The reaction mixture was then stirred at room temperature for a period of 1 h. The consumption of the tetraphenylaluminium ate complex was qualitatively analysed using ^{27}Al NMR employing aluminium nitrate nonahydrate as an external standard.

Typical procedure for the reaction shown in Table 2: Synthesis of phenylcycloheptane (4)



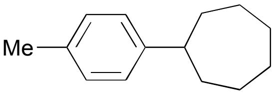
A THF solution of phenylmagnesium chloride (2.20 mL, 1.64 M, 3.60 mmol) was added to a solution of $AlCl_3$ (160 mg, 1.20 mmol) in 1.2 mL of THF at 0 °C. The reaction mixture was stirred at room temperature for a period of 1 h, and then cooled to 0 °C. $FeCl_2(dppbz)_2$ (28.4 mg, 0.03 mmol) was added to the resulting solution at 0 °C, followed by bromocycloheptane (177 mg, 1.00 mmol). The coupling reaction was carried out at 80 °C for 24 h. After cooling the mixture to ambient temperature, aqueous ammonium chloride (saturated, a few drops) and HCl (1 N, 4 mL) were added. The aqueous layer was extracted with ethyl acetate three times (2 mL × 3). The combined organic extracts were filtered using a pad of Florisil (100–200 mesh, Nacalai Tesque Inc.). After removal of the solvent *in vacuo*, the crude product was purified using chromatography on a silica gel to obtain the desired compound (164 mg, 94% yield, >99% purity on GC analysis) as a colourless oil: ^{1}H NMR (270 MHz, $CDCl_3$, δ): 1.50–1.98 (m, 12H, $(CH_2)_6$), 2.64 (tt, J = 3.4, 10.3 Hz, 1H, ArC*H*), 7.12–7.20 (m, 3H, *ortho*-, *para*-Ar*H*), 7.24–7.30 (m, 2H, *meta*-Ar*H*). ^{13}C NMR (67.8 MHz, $CDCl_3$, δ): 27.6 (2C), 28.3 (2C), 37.2 (2C), 47.4, 125.8, 127.0 (2C), 128.6 (2C), 150.4. All the analytical data were in good agreement with values reported in the literature.[2]

Synthesis of (4-methoxyphenyl)cycloheptane (7)



The reaction was carried out according to the typical procedure using a THF solution of (4-methoxyphenyl)magnesium chloride (4.04 mL, 0.89 M, 3.60 mmol) and bromocycloheptane (177 mg, 1.00 mmol). The reaction was carried out at 80 °C for 48 h. The title compound (147 mg, yield = 72%, purity on GC analysis = 99%) was obtained as a pale yellow oil after silica gel column chromatography. ^{1}H NMR δ 1.50–1.98 (m, 12H, $(CH_2)_6$), 2.61 (tt, J = 3.6, 10.1 Hz, 1H, ArC*H*), 3.78 (s, 3H, OC*H*), 6.79–6.85 (m, 2H, C*H*COC*H*), 7.08–7.14 (m, 2H, C*H*CCC*H*). ^{13}C NMR δ 27.5 (2C), 28.3 (2C), 37.4 (2C), 46.5, 55.6, 114.0 (2C), 127.8, 142.7 (2C), 157.8. All the analytical data were in good agreement with values reported in the literature.[3]

Synthesis of (4-methylphenyl)cycloheptane (8)



The reaction was carried out according to the typical procedure using a THF solution of (4-methylphenyl)magnesium chloride (3.28 mL, 1.10 M, 3.60 mmol) and bromocycloheptane (177 mg, 1.00 mmol). Conditions = 80 °C, 48 h. The title compound (147 mg, yield = 72%, purity on GC

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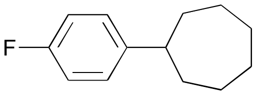
(2) M. Nakamura, K. Matsuo, S. Ito, E. Nakamura, *J. Am. Chem. Soc.*, 2004, **126**, 3686–3687.

(3) G. Cahiez, V. Habiak, C. Duplais, A. Moyeux, *Angew. Chem. Int. Ed.*, 2007, **46**, 4364–4366.

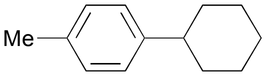
analysis = > 99%) was obtained as a colourless oil after silica gel column chromatography. ^{1}H NMR δ 1.46–1.93 (m, 12H, (C*H*$_2$)$_6$), 2.31 (s, 3H, ArC*H*), 2.63 (tt, *J* = 9.7, 3.5 Hz, 1H, C*H*), 7.05 (brs, 4H, Ar*H*). ^{13}C NMR δ 21.3, 27.5 (2C), 28.3 (2C), 37.3 (2C), 47.0, 126.9 (2C), 129.3 (2C), 135.2, 147.4. All the analytical data were in good agreement with values reported in the literature.[4]

Synthesis of (4-fluorophenyl)cycloheptane (9)



The reaction was carried out according to the typical procedure using a THF solution of (4-fluorophenyl)magnesium chloride (5.08 mL, 0.71 M, 3.60 mmol) and bromocycloheptane (177 mg, 1.00 mmol). Conditions = 80 °C, 48 h. The title compound (109 mg, yield = 56%, purity on GC analysis = 99%) was obtained as a colourless oil after silica gel column chromatography. ^{1}H NMR δ 1.46–1.93 (m, 12H, (C*H*$_2$)$_6$), 2.64 (tt, *J* = 3.3, 9.9 Hz, 1H, ArC*H*), 6.90–6.97 (m, 2H, C*H*CFC*H*), 7.09–7.17 (m, 2H, C*H*CC*H*). ^{13}C NMR δ 27.5 (2C), 28.2 (2C), 37.4 (2C), 46.7, 115.1 (d, *J* = 21.1 Hz, 2C), 128.1 (d, *J* = 7.4 Hz, 2C), 146.0 (d, *J* = 3.2 Hz), 161.2 (d, *J* = 243.0 Hz). All the analytical data were in good agreement with values reported in the literature.[5]

Synthesis of (4-methylphenyl)cyclohexane (10)



The reaction was carried out according to the typical procedure by using a THF solution of (4-methylphenyl)magnesium chloride (3.28 mL, 1.10 M, 3.60 mmol) and bromocyclohexane (163 mg, 1.00 mmol). Conditions = 80 °C, 48 h. The title compound (151 mg, yield = 87%, purity on GC analysis = > 99%) was obtained as a colourless oil after silica gel column chromatography. ^{1}H NMR δ 1.13–1.50 (m, 5H, C*H*C*H*C*H*), 1.71– 1.95 (m, 5H, C*H*C*H*C*H*), 2.31 (s, 3H, ArC*H*$_3$), 2.46 (tt, *J* = 11.5, 2.9 Hz, 1H, ArC*H*), 7.10 (brs, 4H, Ar*H*). ^{13}C NMR δ 21.3, 26.5, 27.3 (2C), 34.9 (2C), 44.5, 127.0 (2C), 129.3 (2C), 135.5, 145.5. All the analytical data were in good agreement with values reported in the literature.[2]

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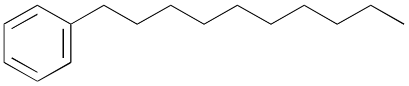
(4) R. Martin, A. Fürstner, *Angew. Chem. Ind. Ed.*, 2004, **43**, 3955–3957.

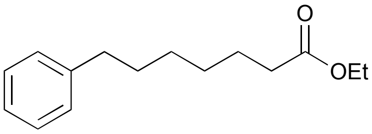
(5) T. Hatakeyama, Y. Kondo, Y. Fujiwara, H. Takaya, S. Ito, E. Nakamura, M. Nakamura, *Chem. Commun.,* 2009, 1216–1218.

Synthesis of phenyldecane (11)



The reaction was carried out according to the typical procedure using a THF solution of phenylmagnesium chloride (2.20 mL, 1.64 M, 3.60 mmol) and 1-bromodecane (221 mg, 1.0 mmol). Conditions = 80 °C, 48 h. The title compound (183 mg, yield = 84%, purity on GC analysis = 97%) was obtained as a colourless oil after silica gel column chromatography. ^{1}H NMR δ 0.89 (t, J = 6.8 Hz, 3H, CH_3), 1.26–1.30 (m, 14H, $(CH_2)_7$), 1.61 (quint, J = 7.6 Hz, 2H, CH_2), 2.60 (t, J = 7.2 Hz, 2H, CH_2), 7.14–7.19 (m, 3H, *ortho-, para*-Ar*H*), 7.25–7.3 (m, 2H, *meta*-Ar*H*). ^{13}C NMR δ 14.5, 23.0, 29.7 (2C), 29.9, 30.0 (2C), 32.3, 36.4, 125.9, 128.6 (2C), 128.7 (2C), 143.0. All the analytical data were in good agreement with values reported in the literature.[6]

Synthesis of ethyl 7-phenylheptanoate (12)



The reaction was carried out according to the typical procedure by using a THF solution of phenylmagnesium chloride (2.20 mL, 1.64 M, 3.60 mmol) and ethyl 7-bromoheptanoate (237 mg, 1.0 mmol). Conditions = 80 °C, 48 h. The title compound (128 mg, yield = 55%, purity on GC analysis = 97%) was obtained as a colourless oil after silica gel column chromatography. ^{1}H NMR δ 1.25 (t, J = 7.3 Hz, 3H, CH_3), 1.32–1.37 (m, 4H, CH_2), 1.54–1.69 (m, 4H, CH_2), 2.28 (t, J = 7.3 Hz, 2H, CH_2CO), 2.60 (t, J = 7.3 Hz, 2H, CH_2Ar), 4.13 (q, J = 7.0 Hz, 2H, OCH_2), 7.14–7.19 (m, 3H, *ortho-, para*-Ar*H*), 7.24–7.30 (m, 2H, *meta*-Ar*H*). ^{13}C NMR δ 14.6, 25.2, 29.2, 29.3, 31.6, 34.7, 36.2, 60.5, 125.9, 128.5 (2C), 128.7 (2C), 143.0, 174.1. All the analytical data were in good agreement with values reported in the literature.[7]

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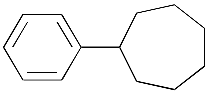
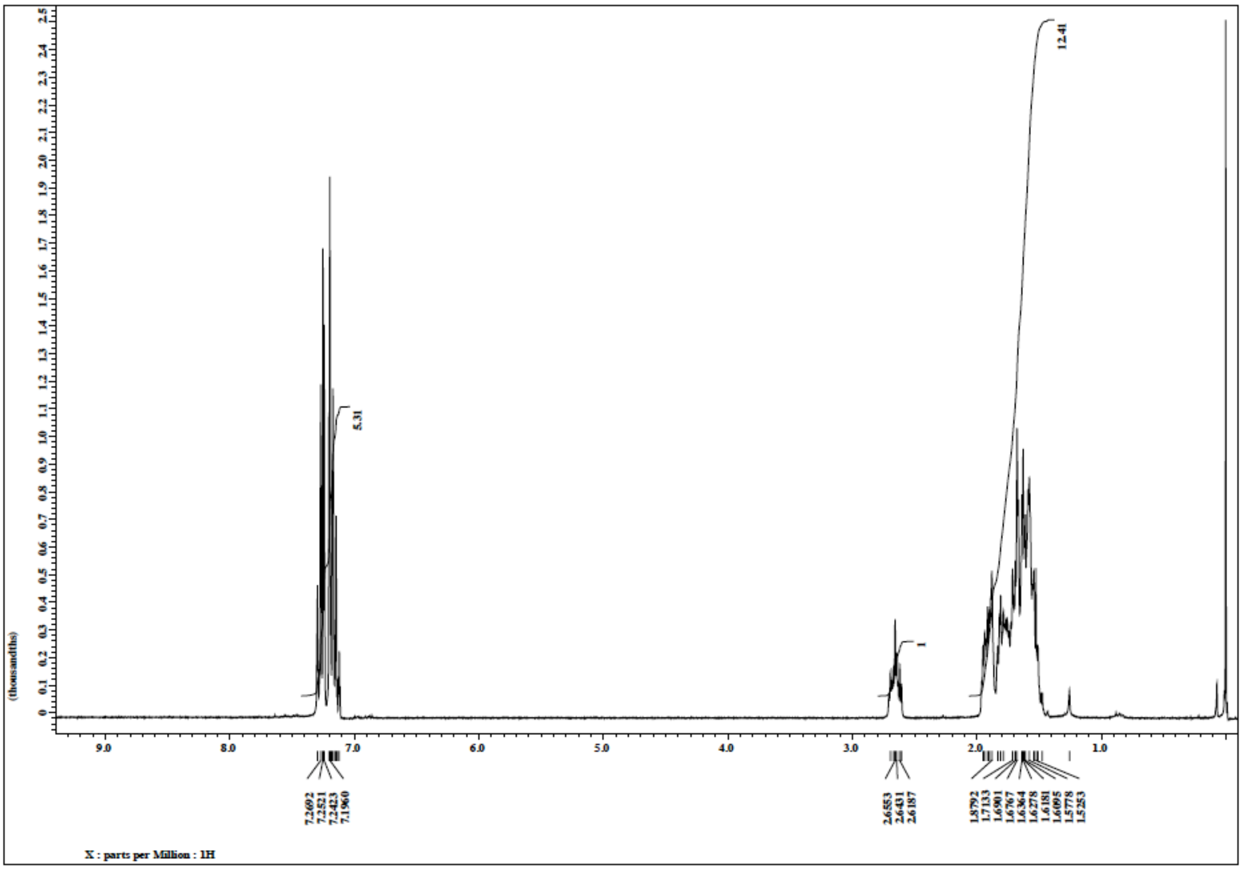
(6) C. M. R. Volla, P. Vogel, *Angew. Chem. Int. Ed.*, 2008, **47**, 1–4.

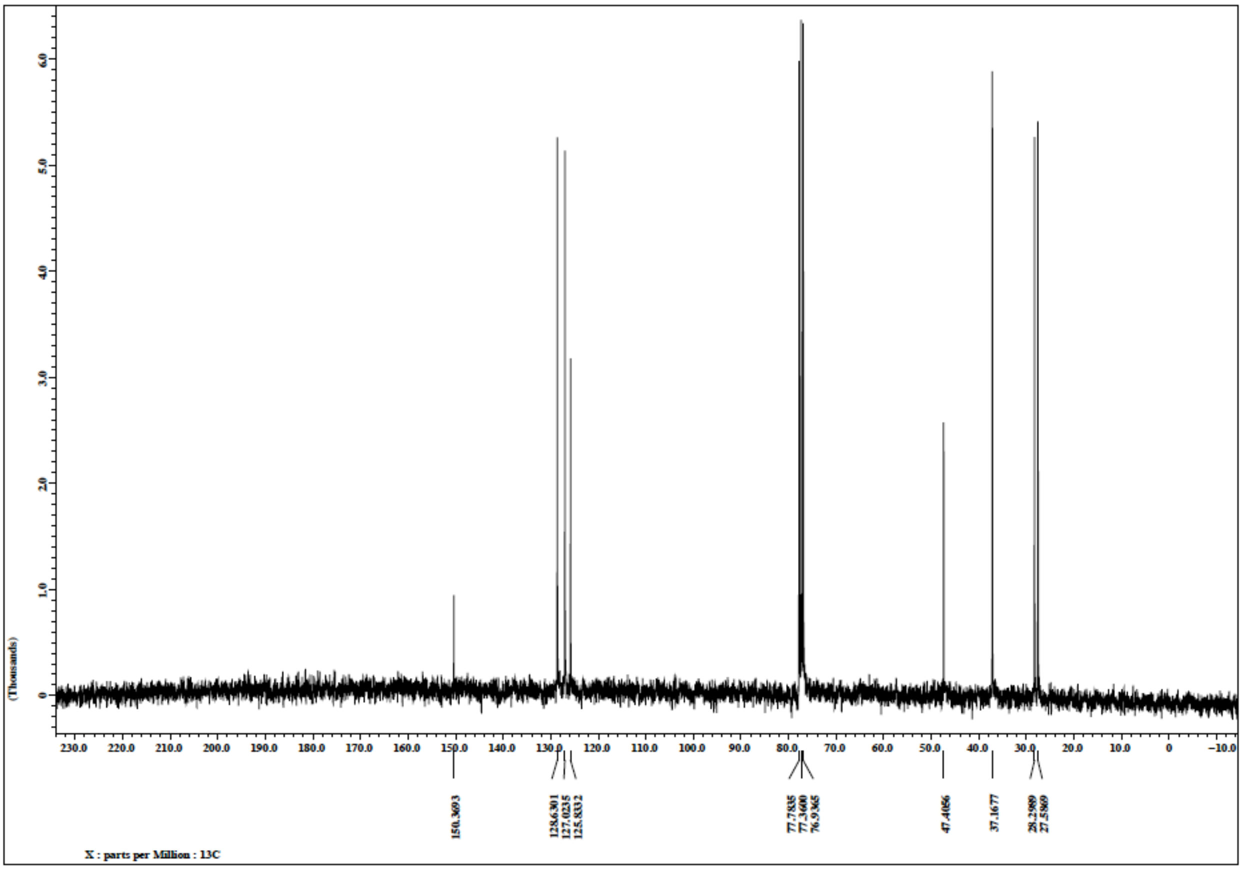
(7) N. Hadei, E. A. B. Kantchev, C. J. O'Brie, M. G. Organ, *J. Org. Chem.*, 2005, **70**, 8503–8507.

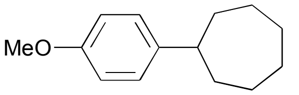
^{1}H and ^{13}C NMR spectra of the compounds



(**4**)



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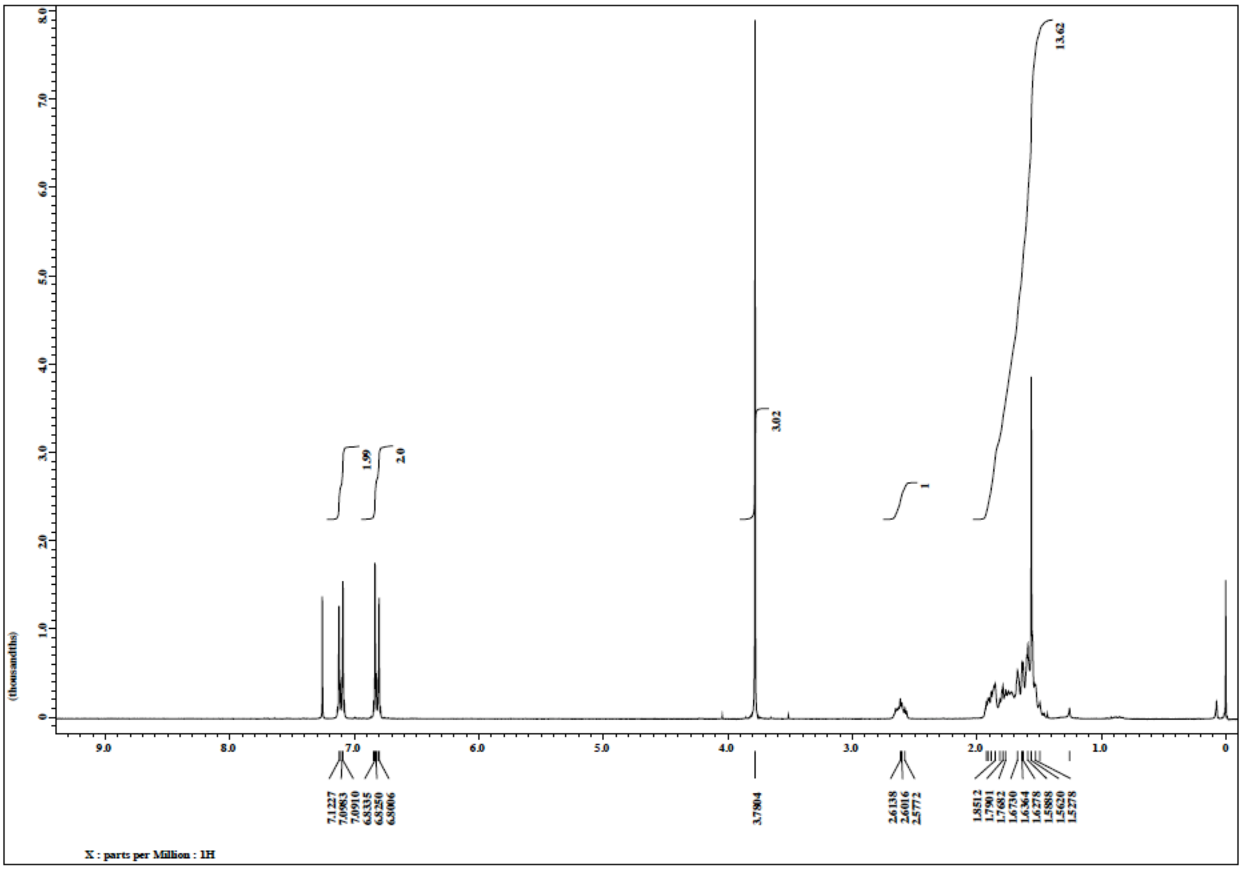
(**7**)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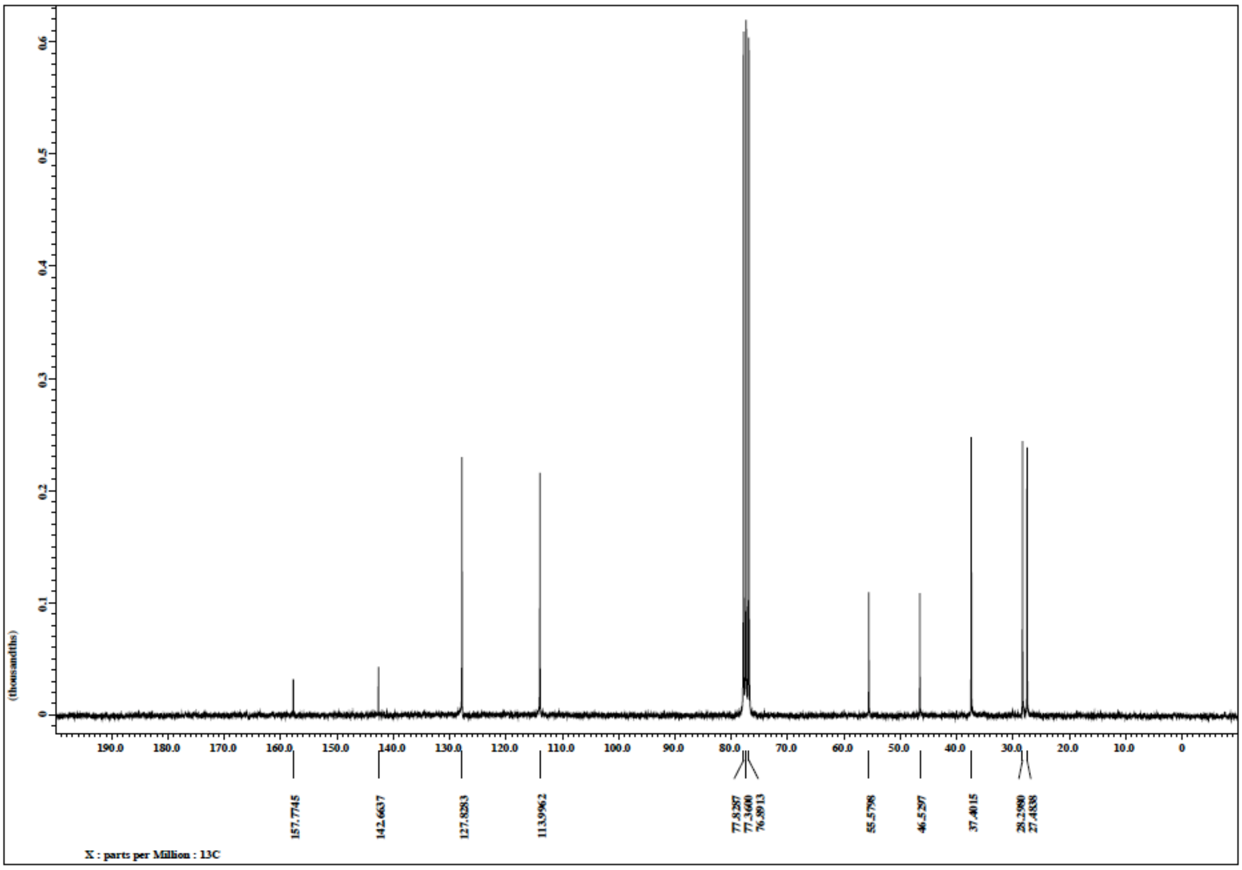
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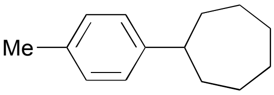
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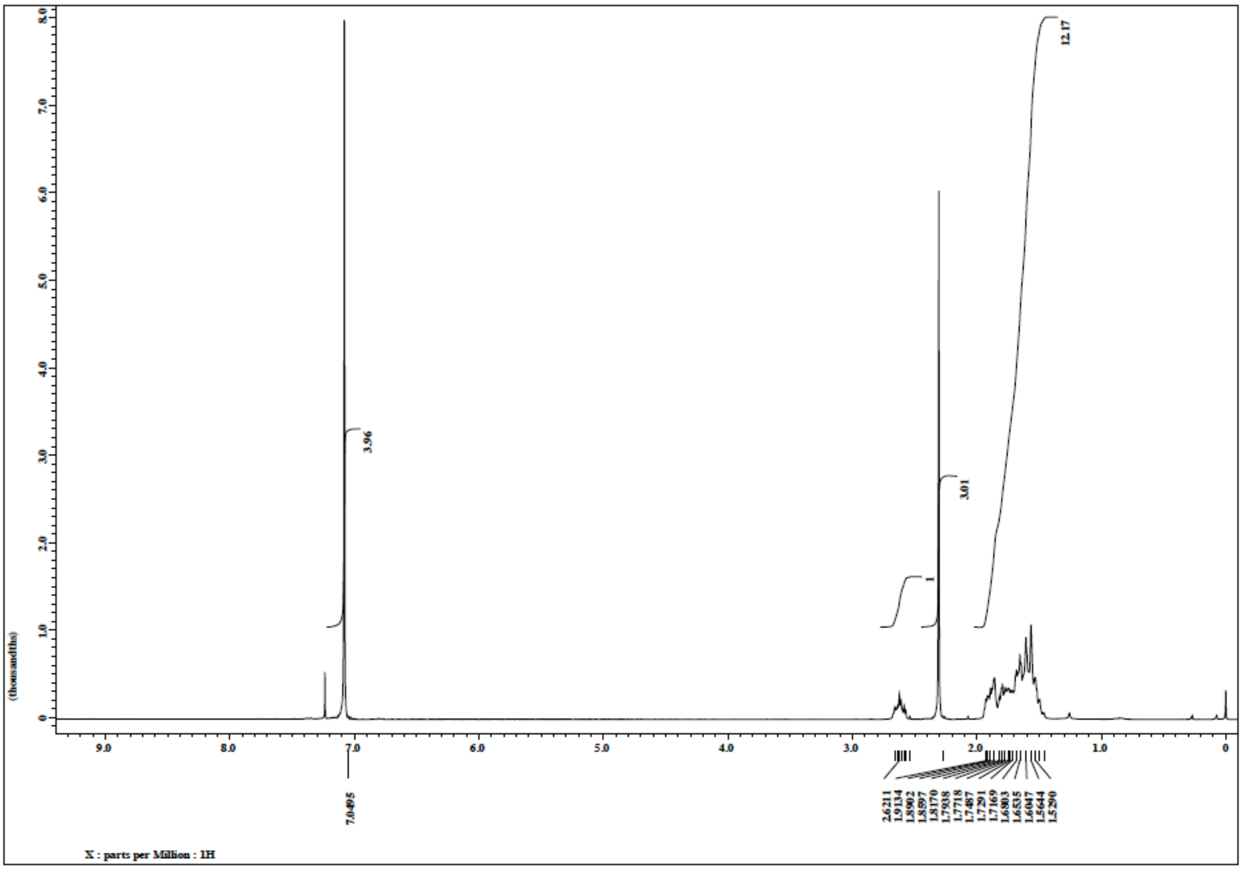
(**8**)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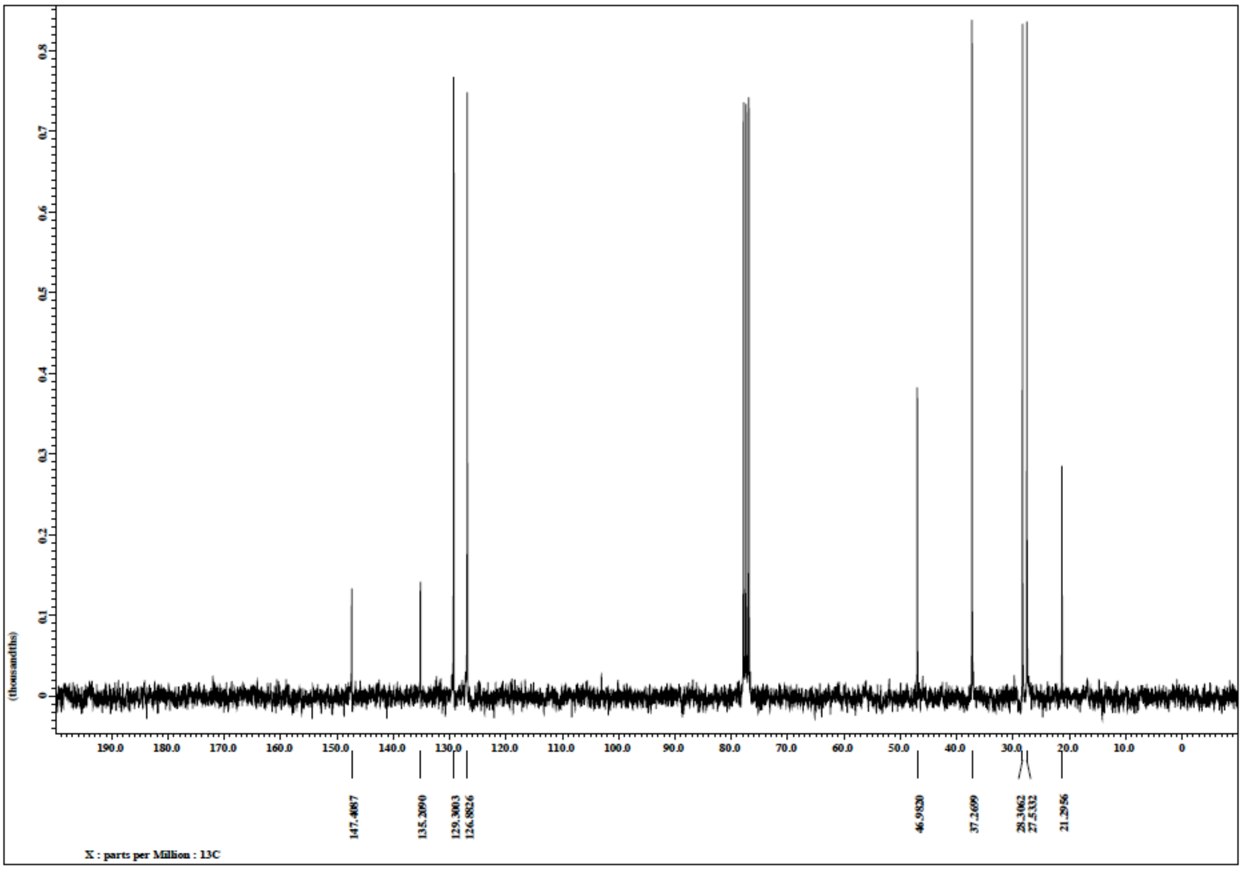
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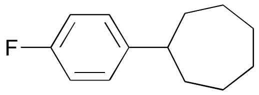
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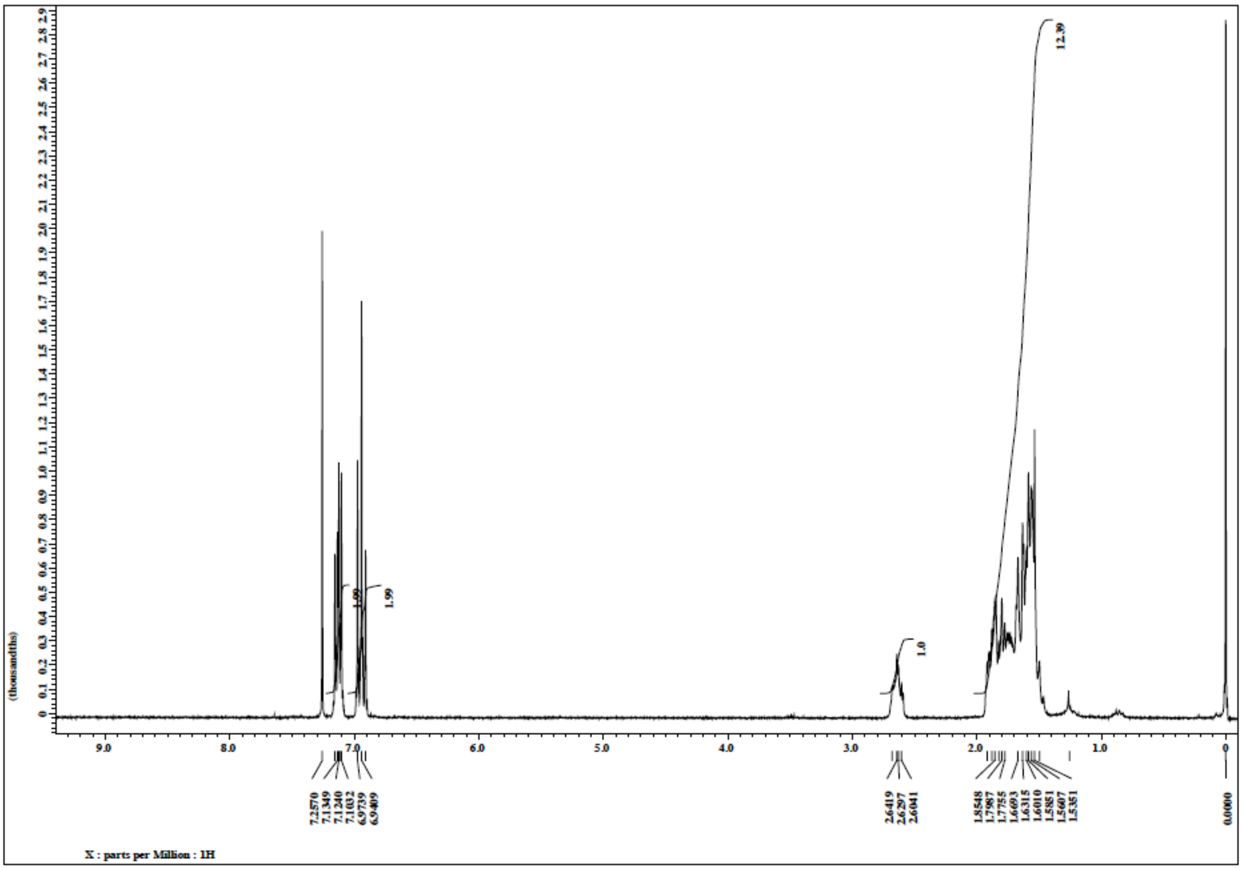
(**9**)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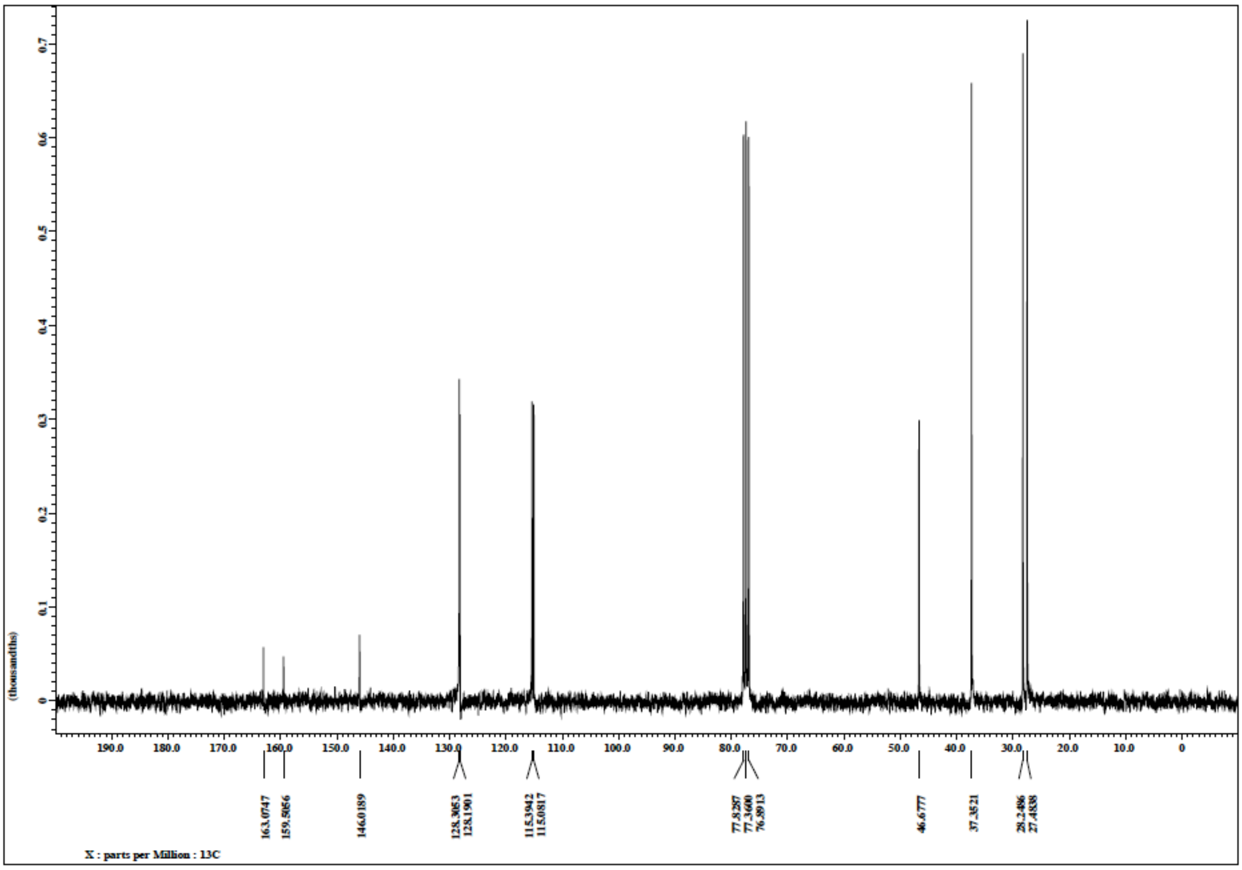
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37.3521
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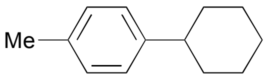
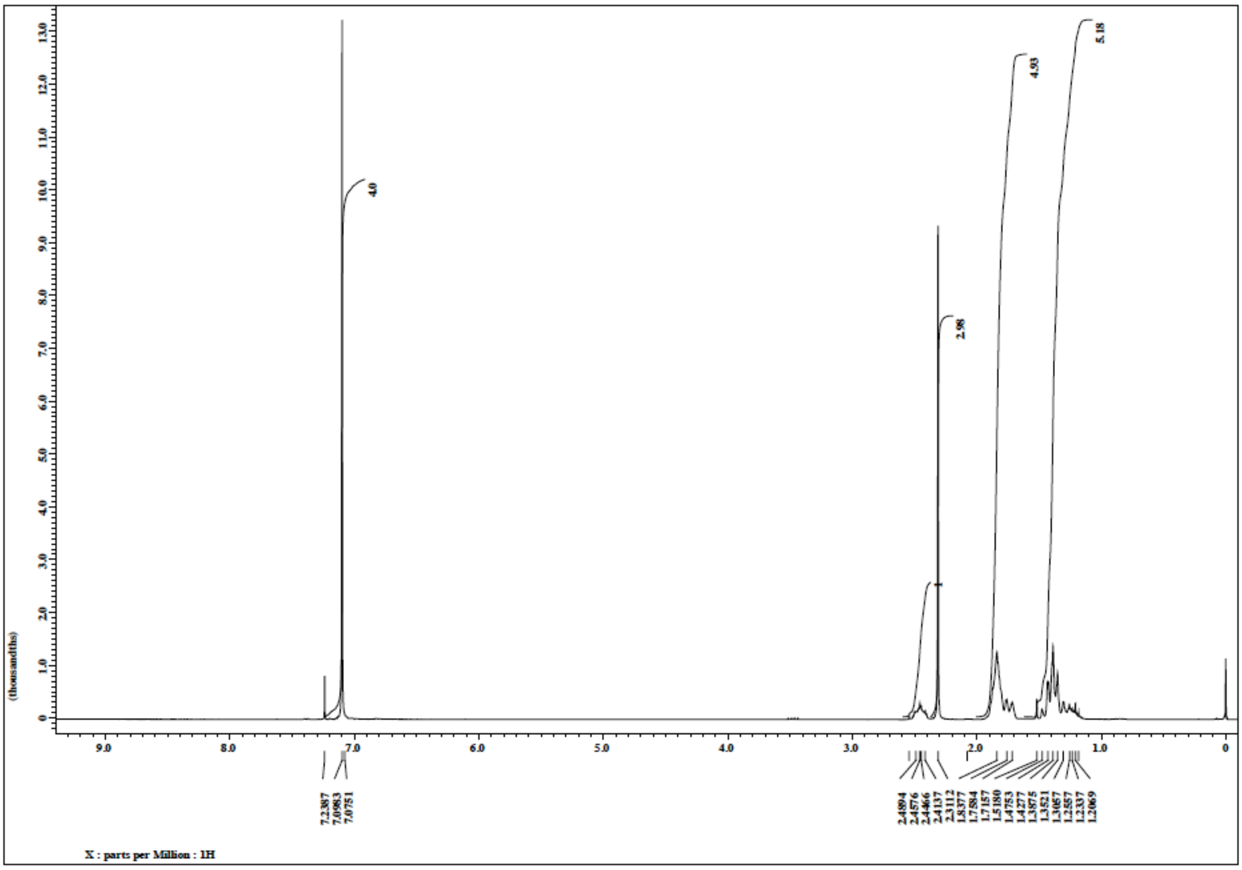
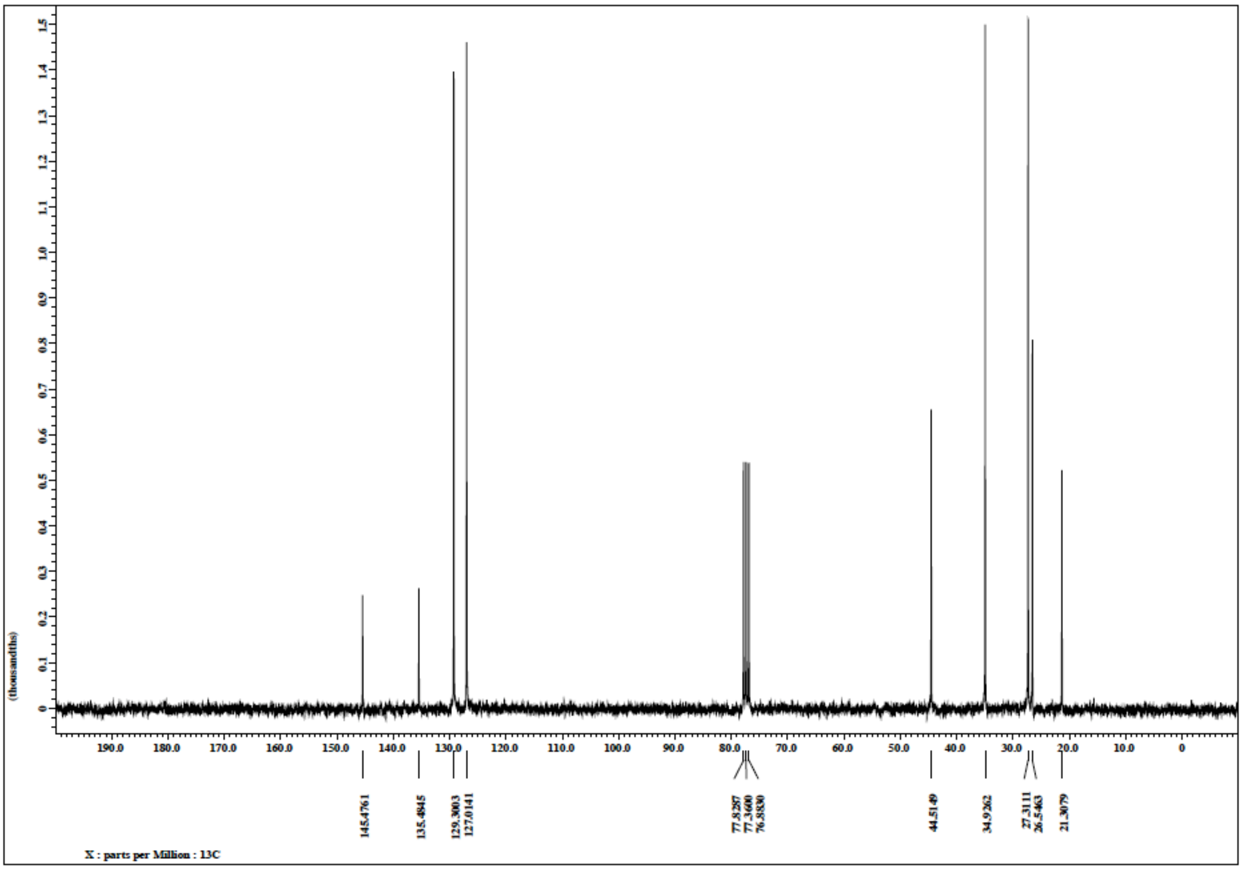
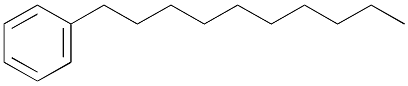
27.4838
X : parts per Million : 13C


Me

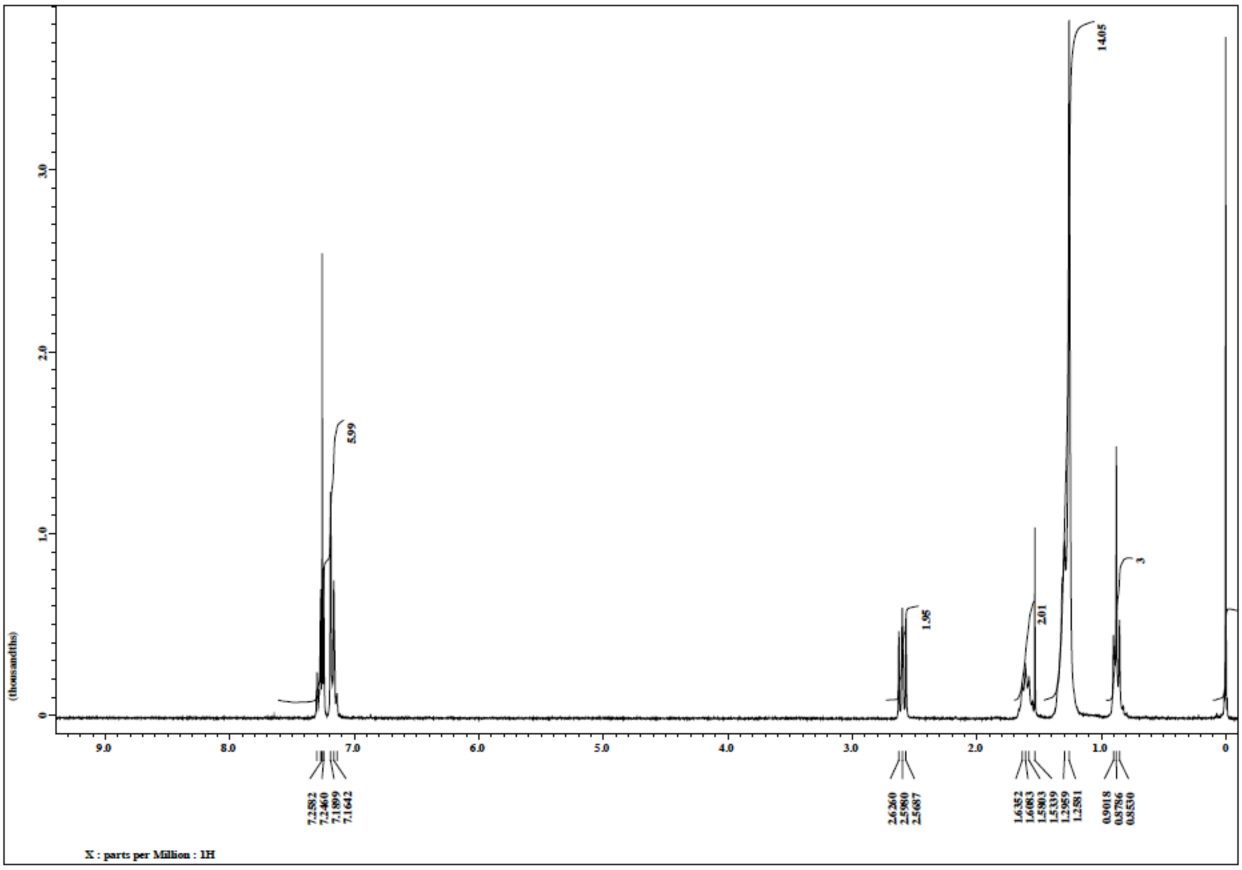
(**10**)


(thousandths)
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
4.0
2.98
4.93
5.18
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2387
7.0983
7.0751
2.4894
2.4576
2.4466
2.4137
2.3112
1.8377
1.7584
1.7157
1.5180
1.4753
1.4277
1.3875
1.3521
1.3057
1.2557
1.2337
1.2069
X : parts per Million : 1H

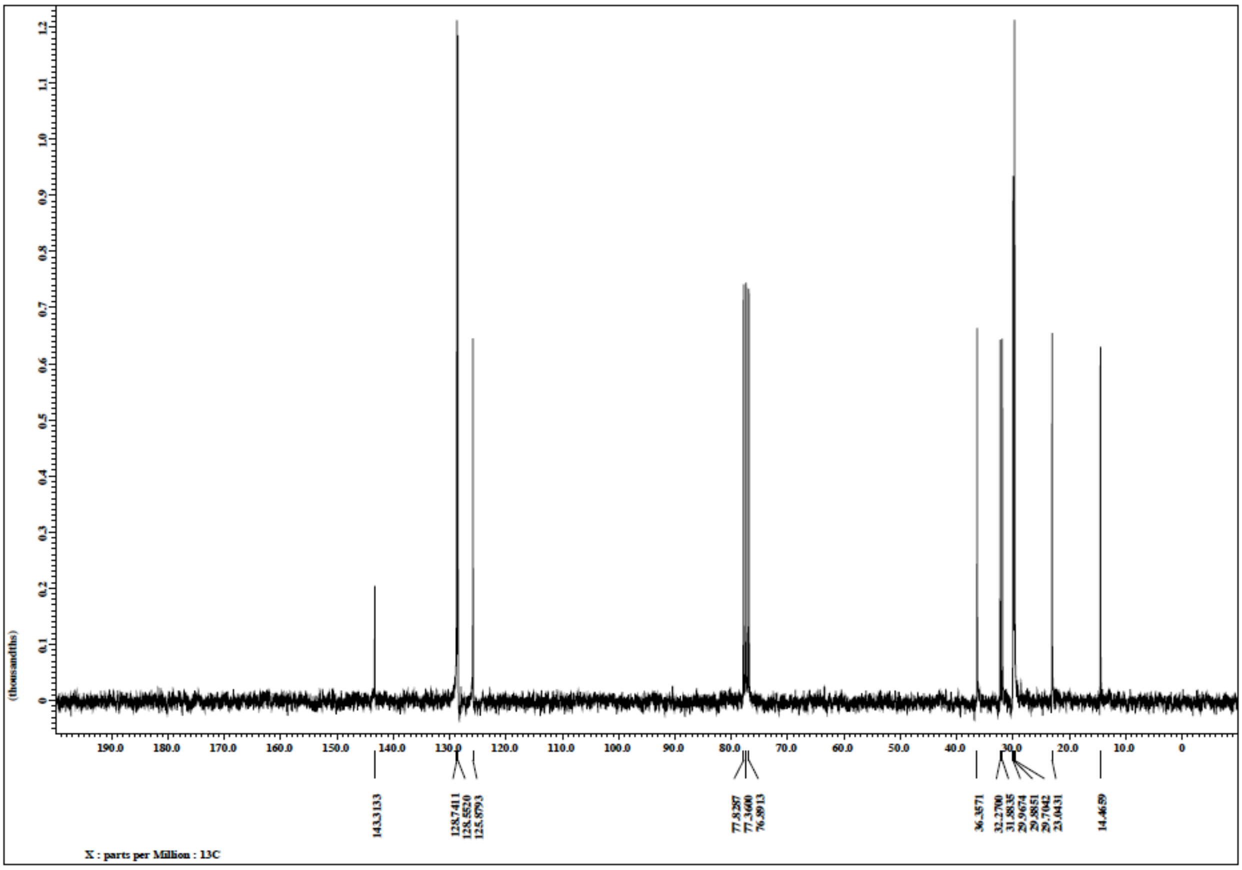

(thousandths)
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
145.4761
135.4845
129.3003
127.0141
77.8287
77.3600
76.8830
44.5149
34.9262
27.3111
26.5463
21.3079
X : parts per Million : 13C



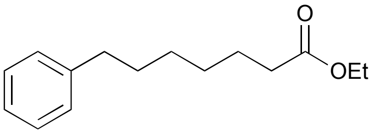
(**11**)



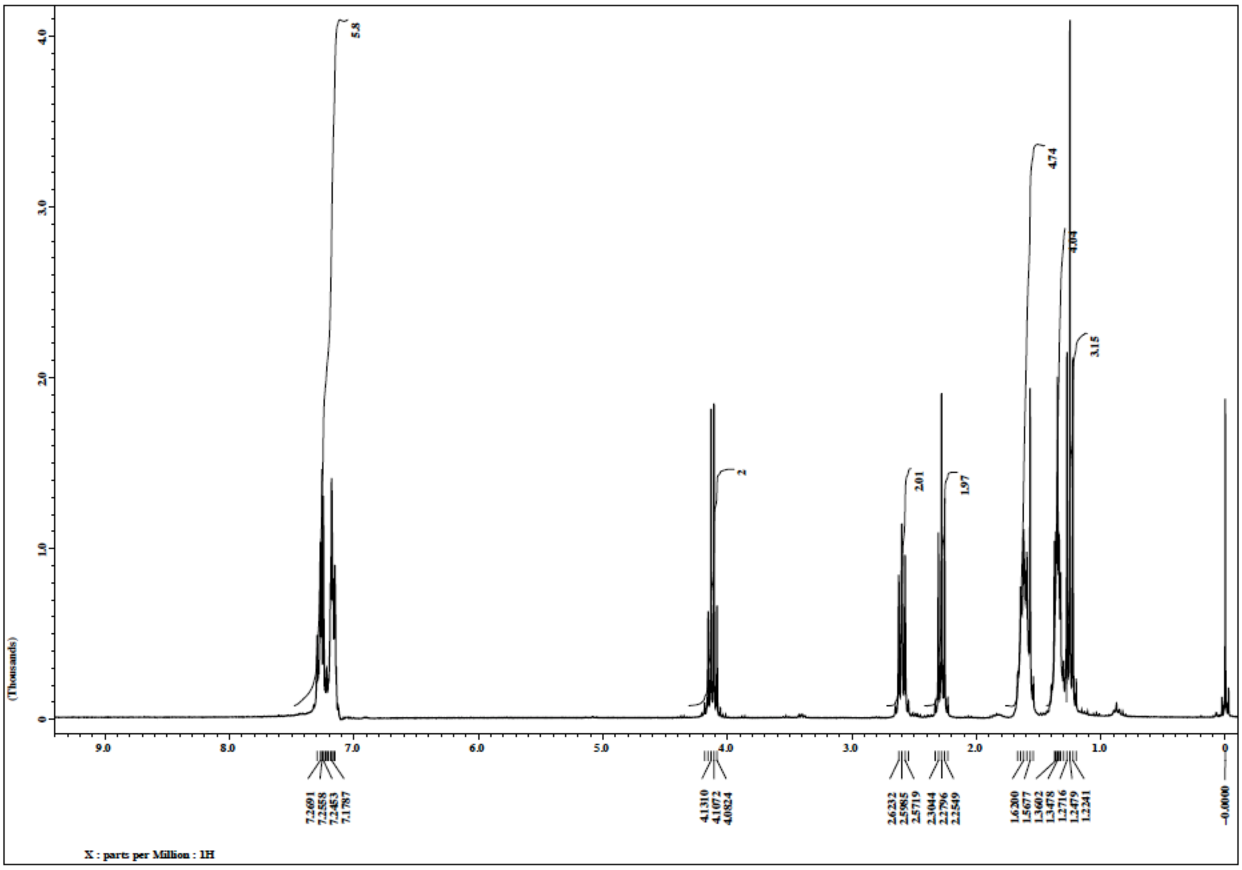
(thousandths)
0
1.0
2.0
3.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
5.99
1.95
2.01
14.05
3
7.2582
7.2460
7.1899
7.1642
2.6260
2.5980
2.5687
1.6352
1.6083
1.5803
1.5339
1.2959
1.2581
0.9018
0.8786
0.8530
X : parts per Million : 1H

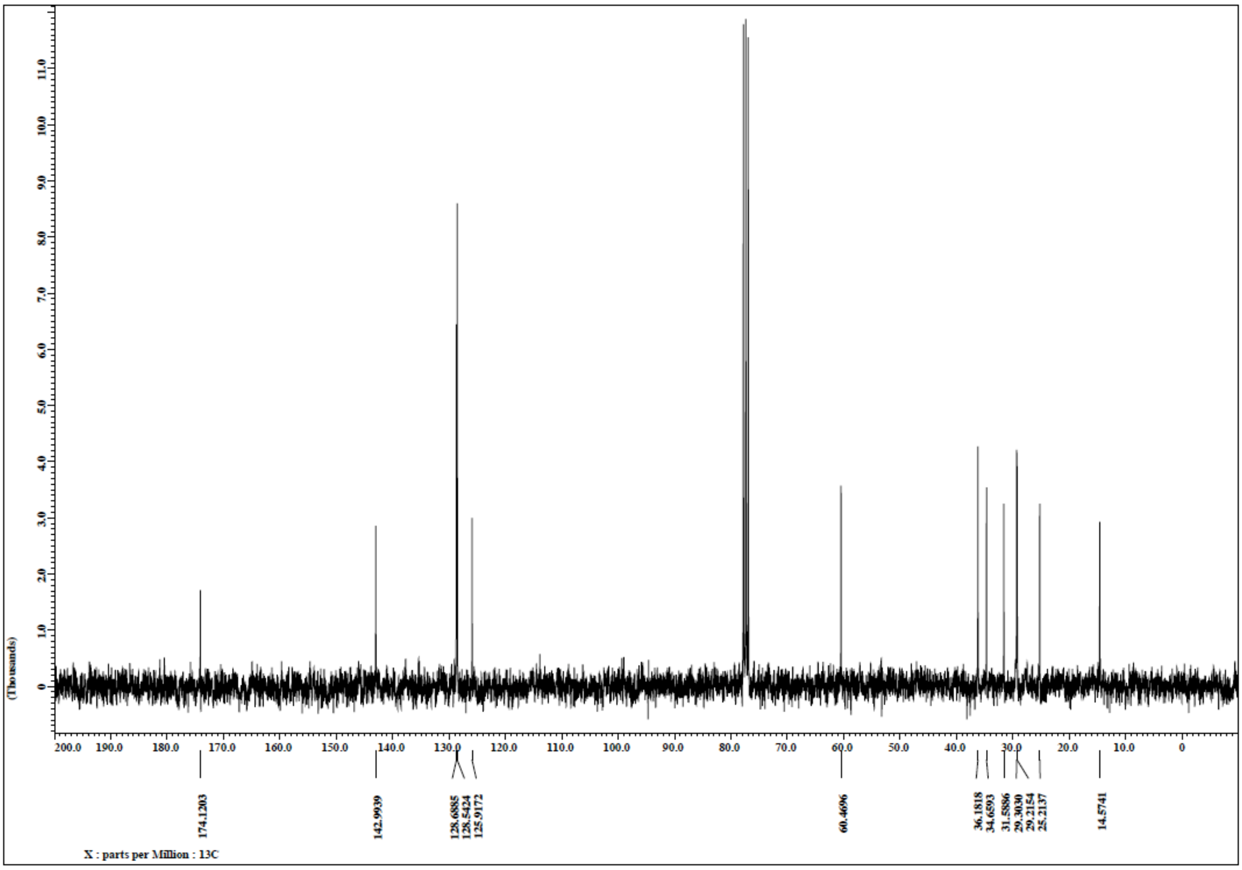


(thousandths)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
143.3133
128.7411
128.5520
125.8793
77.8287
77.3600
76.8913
36.3571
32.2700
31.8835
29.9674
29.8851
29.7042
23.0431
14.4659
X : parts per Million : 13C


O
OEt

(**12**)


(Thousands)
0
1.0
2.0
3.0
4.0
5.8
2
2.01
1.97
4.74
4.04
3.15
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2691
7.2858
7.2453
7.1787
4.1310
4.1072
4.0824
2.6232
2.5985
2.5719
2.3044
2.2796
2.2549
1.6200
1.5677
1.3602
1.3478
1.2716
1.2479
1.2241
-0.0000
X : parts per Million : 1H


(Thousands)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
174.1203
142.9939
128.6885
128.5424
125.9172
60.4696
36.1818
34.6593
31.5886
29.3030
29.2154
25.2137
14.5741
X : parts per Million : 13C