# A Study on Applications of *N*-Substituted Main-Chain NHC-Palladium Polymers as Recyclable Self-Supported Catalysts for

#### the Suzuki–Miyaura Coupling of Aryl Chlorides in Water

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#### **1. General information:**

Starting materials and solvents were purchased from common commercial sources and were used additional purification. The gas chromatography analysis was performed on a GC instrument. <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded from CDCl<sub>3</sub> and DMSO solutions on a Bruker AM 250 spectrometer, using TMS as internal standard.

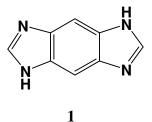
PhCH<sub>3</sub> was distilled from sodium and benzophenone under argon atmosphere prior to use. DMF was distilled under argon. DMSO for polymerization reactions was of reagent quality and used as obtained from commercial sources.

Formic acid was refluxed on Phetalic anhydride for 6h and distilled.

#### 2. Procedure for formation of Benzo-bis(imidazole) 1:

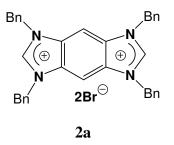
1,2,4,5-Benzenetetraamine tetrahydrochloride (284 mg, 1.00 mmol) was poured into a round bottom flask was charged with a magnetic stir bar. Formic acid (88-99%) was added and the flask was fitted with an air-jacketed condenser. The reaction carried out in an oil bath at 100 °C for 36 h. The reaction mixture was then allowed to cool, decanted into ice-cold water (equal volume to formic acid) and neutralized with K<sub>2</sub>CO<sub>3</sub>. Neutralization caused precipitation of the product which was collected via vacuum filtration, washed with cold water, and dried under vacuum over P<sub>2</sub>O<sub>5</sub>.

The desired product as a light brown solid:; <sup>1</sup>H NMR (250 MHz, DMSO-*d*6, D<sub>2</sub>O)  $\delta$  7.651 (s, 2H), 8.156 (s, 2H); <sup>13</sup>C NMR (250 MHz, DMSO-*d*6)  $\delta$  99.67, 135.38, 143.01.



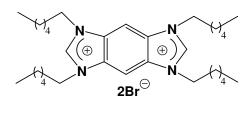
#### **3.** Procedure for formation of Tetrabenzyl benzo-bis(imidazolium) bromide 2a:

In a well-dried two necked 100ml Schlenk flask, bis(imidazole) (576 mg, 3.64 mmol) was added to a solution of NaH (298 mg, 60 wt %, 7.46 mmol) in PhCH<sub>3</sub> (30 mL) under argon atmosphere. The resulting solution was heated to 110 °C for 1 h, after cooling the solution to room temperature, benzylbromide (2.61 mL, 21.84 mmol) was added via syringe. The suspension was placed in an oil bath at 110 °C for 1 h, then dry DMF (30 mL) was added via syringe and the reaction was maintained at 110 °C for 6 h, then 60 °C for 4 h. Upon completion, the suspension was allowed to cool, diluted with PhCH<sub>3</sub> (50 mL) and the solids were collected by vacuum filtration, rinsed with water and THF successively, and dried under vacuum over P<sub>2</sub>O<sub>5</sub> to give a tan powder: <sup>1</sup>H NMR (250 MHz, DMSO-*d*6)  $\delta$  5.828 (s, 8H), 7.341-7.351 (m, 12H), 7.533-7.550 (m, 8H), 8.847 (s, 2H), 10.458 (s, 2H), <sup>13</sup>C NMR (250 MHz, DMSO-*d*6)  $\delta$  50.99, 100.13, 128.9, 129.28, 129.40, 130.73, 133.82, 146.58.



#### 4. Procedure for formation of Tetrahexyl benzo-bis(imidazolium) bromide 2b:

In a well-dried two necked Schlenk flask, bis(imidazole) (475 mg, 3.00 mmol) was added to a solution of sodium hydride (245 mg, 60 wt %, 6.10 mmol) in absolute toluene (10 mL) under argon ambiance. The system was refluxed at 110 °C for 1 h then allowed to cool to room temperature. 1-bromohexane (2.8 mL, 20.00 mmol) was added to reaction mixture via syringe. The resulting mixture was stirred at 110 °C for 2 h, then dry DMF (10 mL) was added via syringe. The reaction was maintained at 110 °C for 10 h, then 60 °C for 6 h. The reaction mixture allowed cooling to room temperature. Then the concentrated suspension in vacuum was added to 1:1 CH<sub>2</sub>Cl<sub>2</sub>/MeOH. After removal of insoluble NaBr, to the resultant oil was added ethyl acetate until precipitation of the product occurred. The solids were collected via vacuum filtration and dried under vacuum to provide 1.71 g (86%) of the product as a light pink powder. <sup>1</sup>H NMR (250 MHz, DMSO-*d*6)  $\delta$  10.291 (s, 2H), 9.162 (s, 2H), 4.624 (t, *J* = 7.5Hz, 8H), 1.969 (p, 8 H), 1.291(m, 24H), 0.822 (t, *J* = 6.7Hz, 12H); <sup>13</sup>C NMR (250 MHz, DMSO-*d*6)  $\delta$  145.98, 130.59, 99.62, 47.80, 31.12, 28.75, 25.83, 22.36, 14.28.

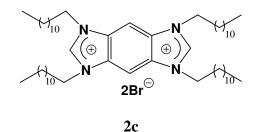


**2**b

#### 5. Procedure for formation of Tetradodecyl benzo-bis(imidazolium) bromide 2c:

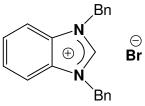
In a well-dried two necked 100ml Schlenk flask, bis(imidazole) (475 mg, 3.00 mmol) was added to a solution of NaH (245 mg, 60 wt %, 6.10 mmol) in PhCH<sub>3</sub> (15 mL) under argon atmosphere. The resulting solution was heated to 110 °C for 1 h, after cooling the solution to room temperature, 1-bromododecane (4.8 mL, 20.00 mmol) was added via syringe. The suspension was placed in an oil bath at 110 °C for 1 h, then dry DMF (10 mL) was added via syringe and the reaction was maintained at 110 °C for 12 h, then 60 °C for 8 h. Upon completion, the suspension was allowed to cool. Then the concentrated suspension in vacuum was added to 2:1 CH<sub>2</sub>Cl<sub>2</sub>/MeOH. After removal of insoluble NaBr, to the resultant oil was added ethyl acetate until precipitation of the product occurred. The solids were collected via vacuum filtration and dried under vacuum over P<sub>2</sub>O<sub>5</sub> to give 2.31 g (77%) of the product as a light pink powder. vacuum: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>-d6)  $\delta$ 

10.076 (s, 2H), 9.534 (s, 2H), 4.933 (t, J = 6.35Hz, 8H), 1.984 (p, 8H), 1.247-1.353 (m, 80H), 0.899 (t, J = 6.9Hz, 12H), <sup>13</sup>C NMR (250 MHz, CDCl<sub>3</sub>-d6)  $\delta$  14.06, 22.63, 26.47, 29.05, 29.30, 29.43, 29.50, 29.57, 29.59, 31,86, 48.97, 100.71, 129.729, 144.86.

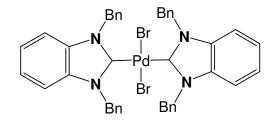


**6. Typical procedure for polymerization 3a-c:** Bis(imidazolium) bromide (1.0 mmol) was dissolved in DMSO (5ml, ca. 0.2 M) and either  $Pd(OAc)_2$  (1.0 eqv, 112 mg), was added in one portion. The solution was placed in a preheated oil bath at 110 °C and stirred open-air for 5-10 h. The reaction mixtures typically darkened in color (to orange-brown) as the reaction progressed. The cooled reaction mixture was added to H<sub>2</sub>O. The result precipitated polymer were collected via vacuum filtration and dried under vacuum.

7. Procedure for formation of 1,3-Dibenzylbenzimidazolium Bromide<sup>1</sup>: NaOH (1.60 mL, 10 mmol) was added to a suspension of Benzimidazole (1.182 g, 10 mmol) in dry CH<sub>3</sub>CN (20 mL). The resulting mixture was stirred for 1 h, then benzylbromide (1.20 mL, 10.00 mmol) was added via syringe. The was placed in an oil bath at 110 °C for 24 h, and the solvent was removed. The residue was dissolved in THF, and insoluble NaBr was filtered off before the solvent was removed in vacuo. The resulting residue was dissolved in toluene (30 mL), and another portion of benzyl bromide (1.20 mL, 10 mmol) was added. The reaction mixture was stirred overnight at 80 °C. The white precipitate formed was filtered off and washed with toluene and diethyl ether. <sup>1</sup>H NMR (250 MHz, DMSO-d6):  $\delta$ =10.23 (s, 1 H), 7.97 (dd, 2 H), 7.60 (dd, 2 H), 7.57–7.52 (m, 4 H), 7.43–7.38 (m, 6 H), 5.82 (s, 4 H). <sup>13</sup>C NMR (63 MHz, DMSO-d6):  $\delta$ = 143.2, 134.3, 131.5, 129.5, 129.2, 128.8, 127.2, 114.5, 52.5.



8. Procedure for formation of  $(1,3-dibenzylbenzimidazole-2-ylidene)_2PdBr_2$  4: Pd(OAc)<sub>2</sub> (224 mg, 1.00 mmol) and 1,3-Dibenzylbenzimidazolium Bromide (760 mg, 2.00 mmol) were dissolved in 30 mL of THF in a two-necked flask under argon atmosphere. After refluxing for 3-5 h and cooling to room temperature, the mixture was filtered through a pad of silica gel. The solvent was removed under vacuo to give a yellow solid. The product was separated by column chromatography. <sup>1</sup>H NMR (400 MHz, DMSO-*d*6): δ=7.64 (8 H), 7.44 (4 H), 7.39–7.26 (4 H), 7.43–7.38 (12 H), 6.10 (s, 8 H). <sup>13</sup>C NMR (63 MHz, DMSO-*d*6): δ= 175.0, 136.3, 134.3, 129.8, 128.9, 128.5, 128.3, 123.8, 60.4.



**9.** General procedure for the Suzuki-Miyaura reaction catalyzed by 3a-c catalysts: A mixture of phenylboronic acid (1.1-1.2 mmol), potassium carbonate (415 mg, 3 mmol) complex **3a-c**, aryl halides (1 mmol) and distilled water (3 ml) under atmosphere of argon was heated with stirring. After the reaction, the reaction solution was cooled to room temperature and the resulted suspend was extracted four times with diethyl ether (4×10 ml). The organic phase was separated and dried over MgSO<sub>4</sub>, and diethyl ether was evaporated under reduced pressure. The final biaryl product was isolated by column chromatography and identified by gas chromatography (GC) and nuclear magnetic resonance spectroscopy (NMR).

**10.** Procedure for reusability test of 3c catalyst. The 3c polymer (0.05 mol % Pd and a mixture of 4-chlorobenzaldehyde (10 mmol), phenylboronic acid (11 mmol), and  $K_2CO_3$  (4.15 g, 30 mmol) in distilled water (30 mL) were placed in an oil bath at 80°C. After the first use of the catalyst 3c to yield 95% of 4-phenylbenzaldehyde (Isolated yield), the catalyst was separated and thoroughly washed with deionized water and EtOH and died at 40 °C under vacuum. The recovered materials were then successfully used in the same way in 7 reaction cycles.

## 11. General procedure for the study of the effects of Hg(0), poly-(4-vinylpyridine) (PVP), and SBA-propyl-SH on the 3a reactivity:

A solution of phenylboronic acid (5.5 mmol) 3-bromoacetophenone (5.0 mmol),  $K_2CO_3$  (15 mmol), and poisoning agent (400 equivalent to total palladium content) in distilled water (12 mL) was magnetically stirred at 60 °C. Then catalyst **3a** (containing 0.0005 mol % Pd) was rapidly added and the reaction progress was monitored by GC.

**12. General Remarks concerning sampling for kinetic studies:** In order to perform these samplings, we have done the reactions in 20 mmol scale and the samples drawn out as low as ~0.1-0.2 mL volume using a large number of disposable plastic syringes in 30 seconds intervals.

**13. Analysis of the polymers by gel permeation chromatography.** The molecular weight of the polymers was determined by Gel-Permeation Chromatography (GPC) technique (Column Waters, 10000 Å-DVB, a refractive index detector and, DMF as eluent). The m olecular weight of the polymers was summarized in Table 1.

Catalyst	Mw (Da.)
3a	136584
Recovered 3a	105452
3b	88459
Recovered 3b	84749
3с	85862
Recovered 3c	130776

Table 1S. The molecular weight of the polymers

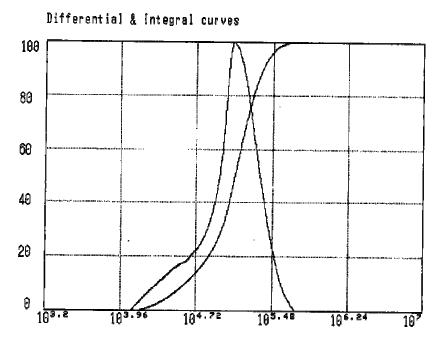


Figure 1S-1. Molecular weight of the organometallic polymer 3a

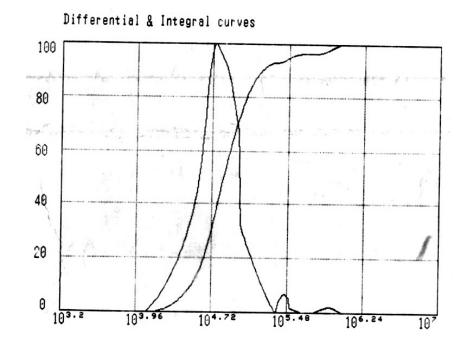


Figure 1S-2. Molecular weight of the recovered organometallic polymer 3a

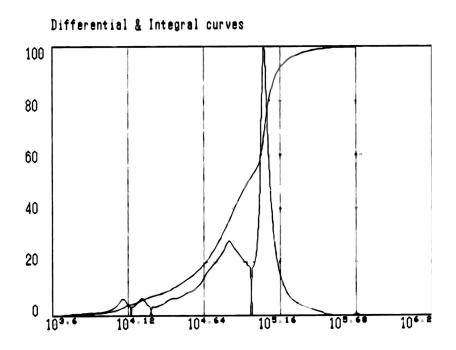


Figure 1S-3. Molecular weight of the organometallic polymer 3b

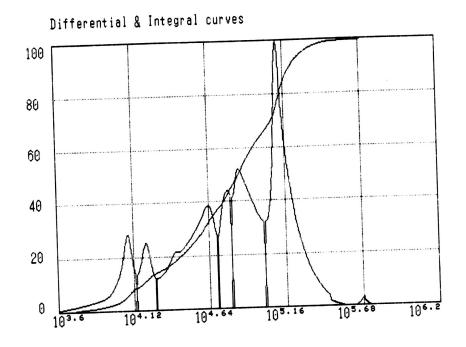


Figure 1S-4. Molecular weight of the recovered organometallic polymer 3b

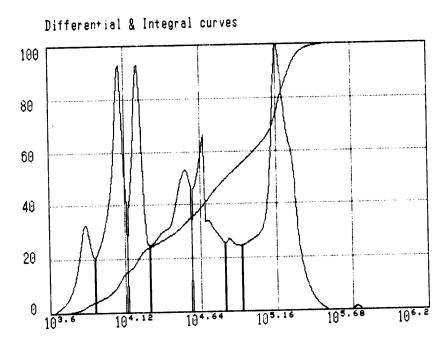


Figure 1S-5. Molecular weight of the organometallic polymer 3c

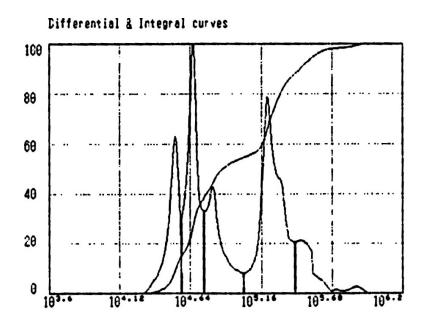


Figure 1S-6. Molecular weight of the recovered organometallic polymer 3c

11.1 **Dynamic laser light scattering:** The dynamic laser light scattering experiments were performed with the aqueous solution of catalyst **3a** (0.0005 mol%) in the reaction condition (A solution of phenylboronic acid (1.1 mmol) 3-bromoacetophenone (1.0 mmol),  $K_2CO_3$  (3 mmol) in distilled water (3 mL)) at scattering angle of 90°.

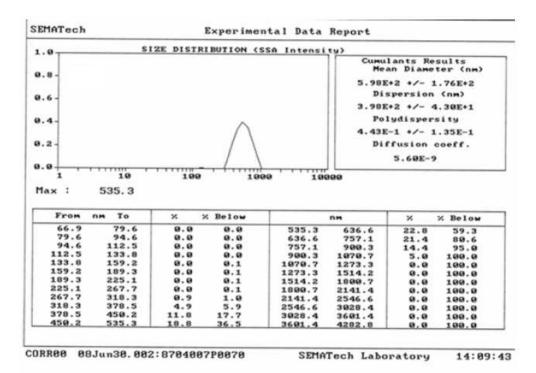
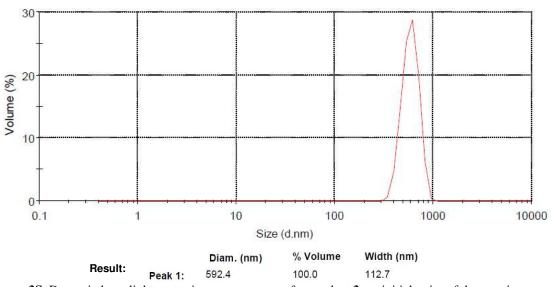
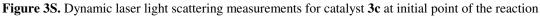


Figure 2S. Dynamic laser light scattering measurements for catalyst 3a

11.2 **Dynamic laser light scattering:** The dynamic laser light scattering experiments were performed with the aqueous solution of catalyst **3a** (0.0005 mol%) in the reaction condition (A solution of phenylboronic acid (1.1 mmol) 3-bromoacetophenone (1.0 mmol),  $K_2CO_3$  (3 mmol) in distilled water (3 mL)) at scattering angle of 60°.

Size Distribution by Volume





Size Distribution by Volume

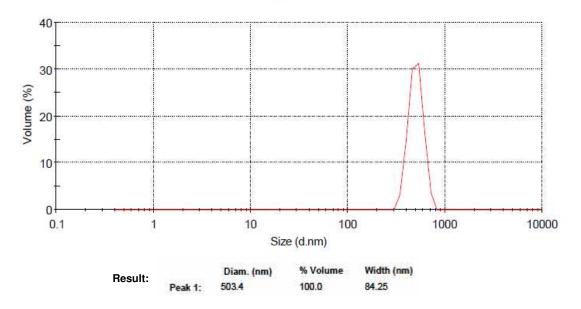


Figure 4S. Dynamic laser light scattering measurements for catalyst 3c after 2 hours

Size Distribution by Volume

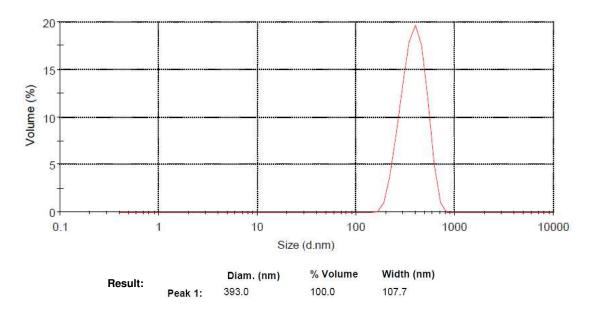
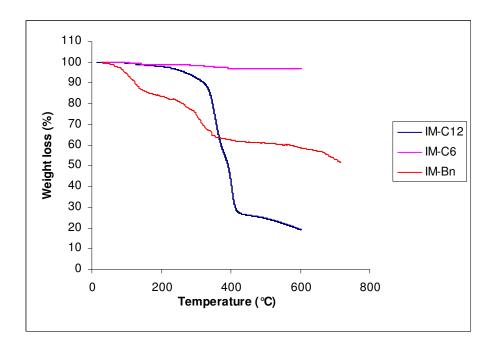
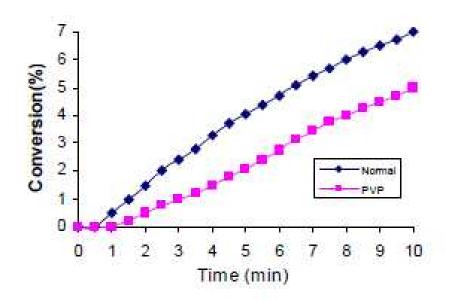


Figure 5S. Dynamic laser light scattering measurements for catalyst 3c after 8 hours

#### 12. Thermal gravimetric analysis (TGA) of polymers 3

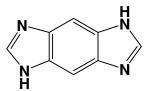


**Figure 6S.** Thermal gravimetric analysis (TGA) of polymers 3. This data significantly shows the high thermal stability of this main chain organometallic polymer.

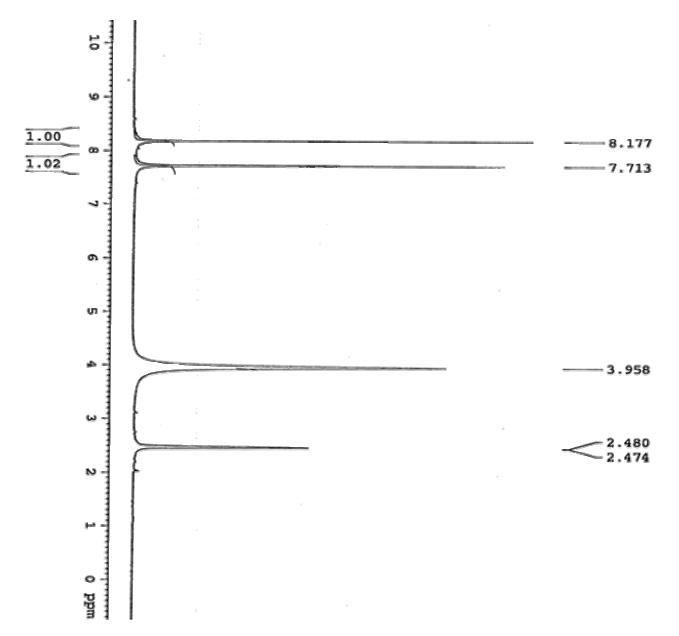


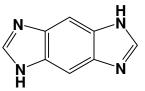
**Figure 7S.** Induction period of Suzuki coupling reaction of 3-bromoacetophenone with phenylboronic acid by using **3c** under normal (blue square), and in the presence of 400 equiv. PVP (pink square) catalyst in water

13. <sup>1</sup>H and <sup>13</sup>C-NMR spectra data.

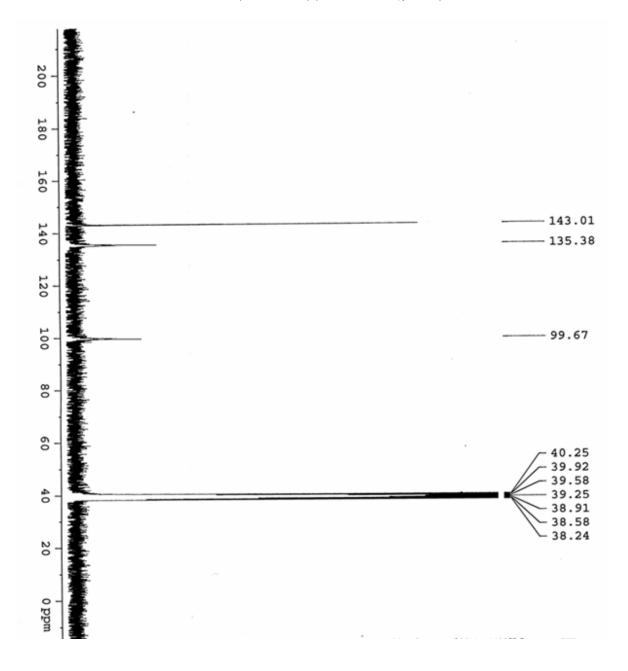


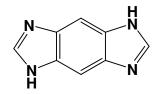
Benzo-bis(imidazole)(in DMSO-d<sub>6</sub>, D<sub>2</sub>O)



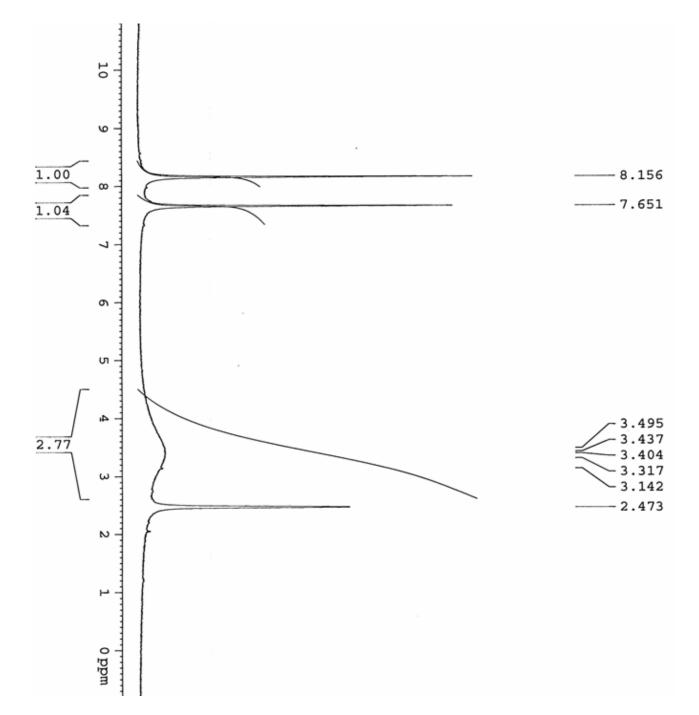


Benzo-bis(imidazole)(in DMSO-d<sub>6</sub>, D<sub>2</sub>O)



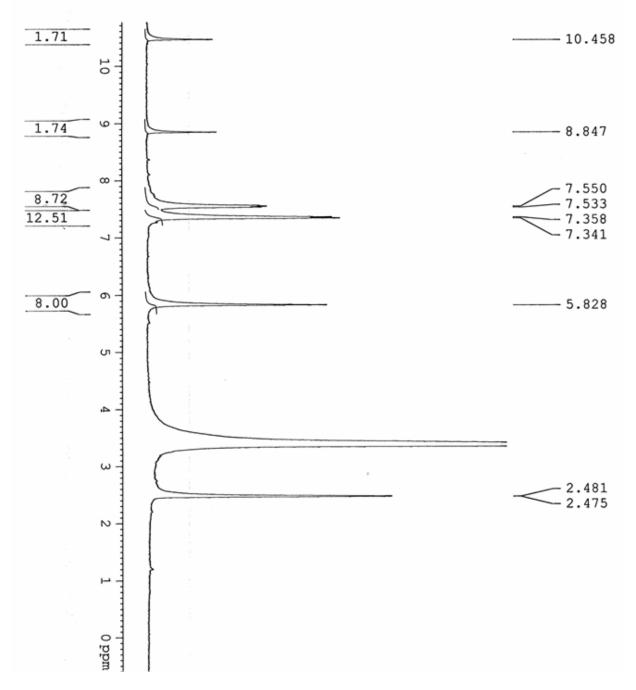


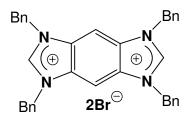
Benzo-bis(imidazole)(in DMSO-d<sub>6</sub>)



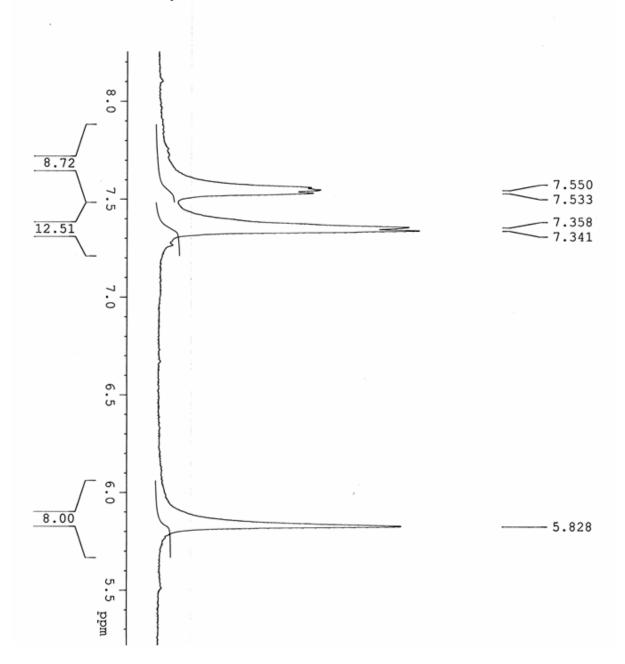


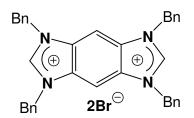
Tetrabenzyl benzo-bis(imidazolium) bromide (in DMSO-d<sub>6</sub>)

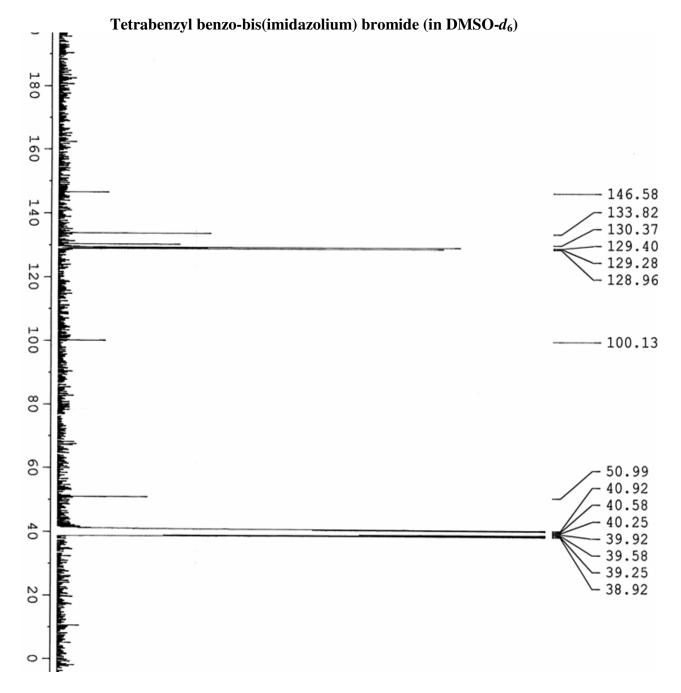


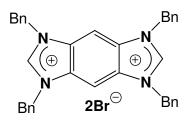


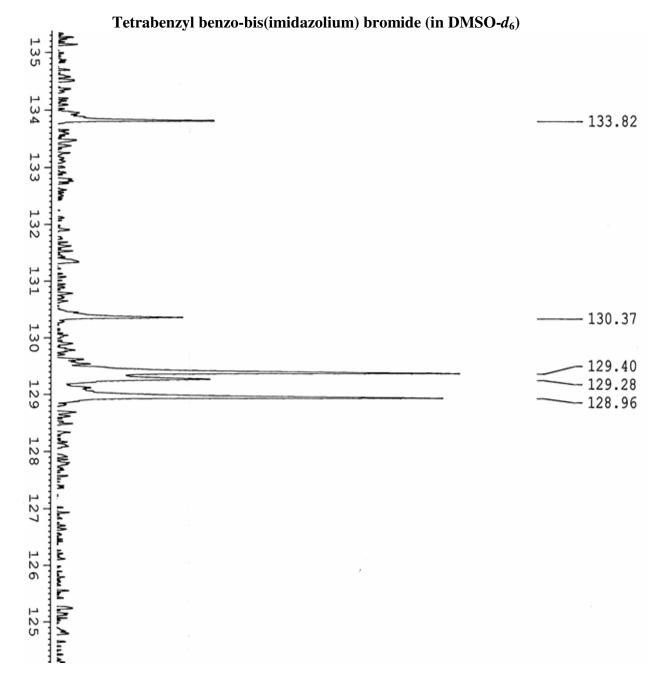
Tetrabenzyl benzo-bis(imidazolium) bromide (in DMSO-d<sub>6</sub>)

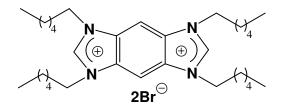




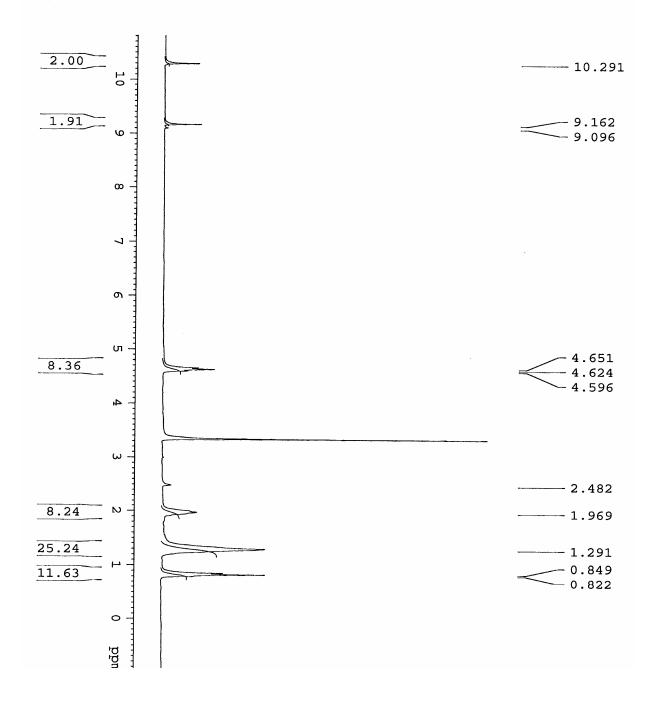






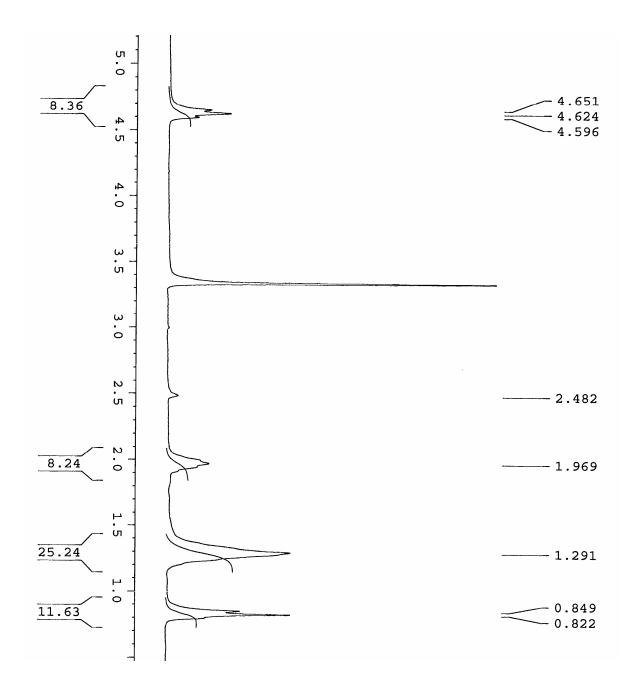


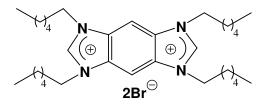
Tetrahexyl benzo-bis(imidazolium) bromide (in DMSO-d<sub>6</sub>)



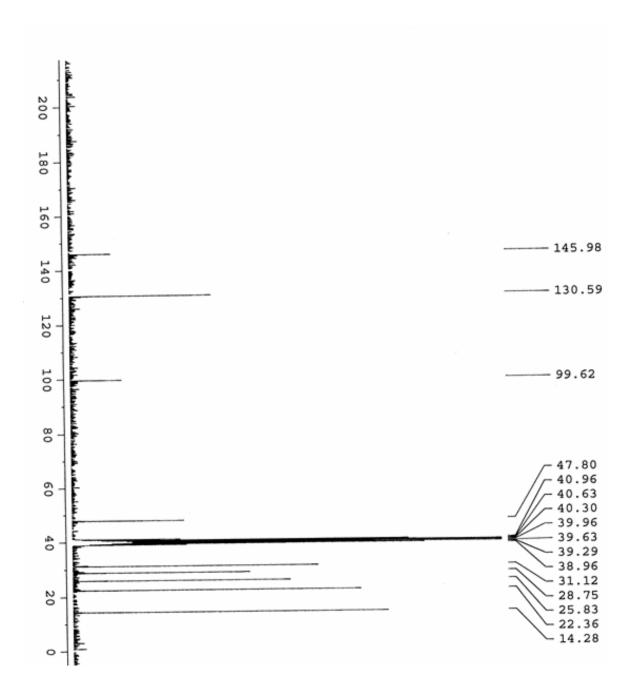


Tetrahexyl benzo-bis(imidazolium) bromide (in DMSO-d<sub>6</sub>)



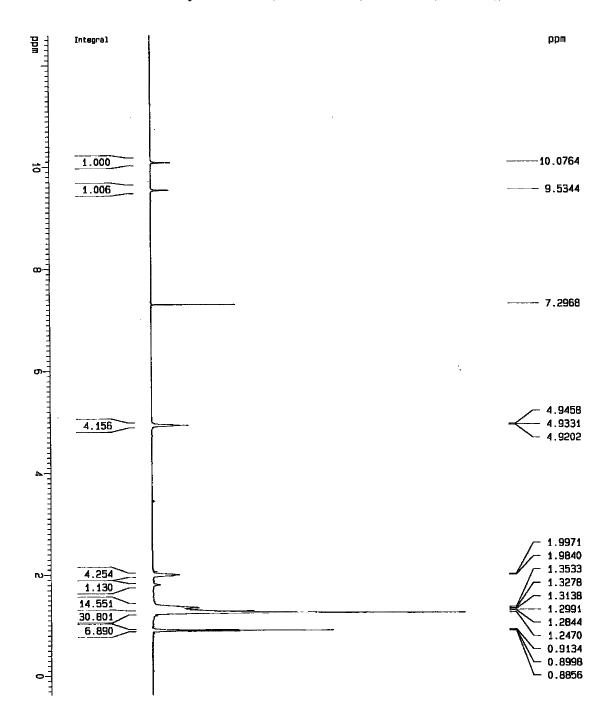


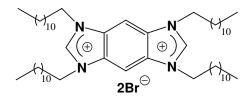
Tetrahexyl benzo-bis(imidazolium) bromide (in DMSO-d<sub>6</sub>)

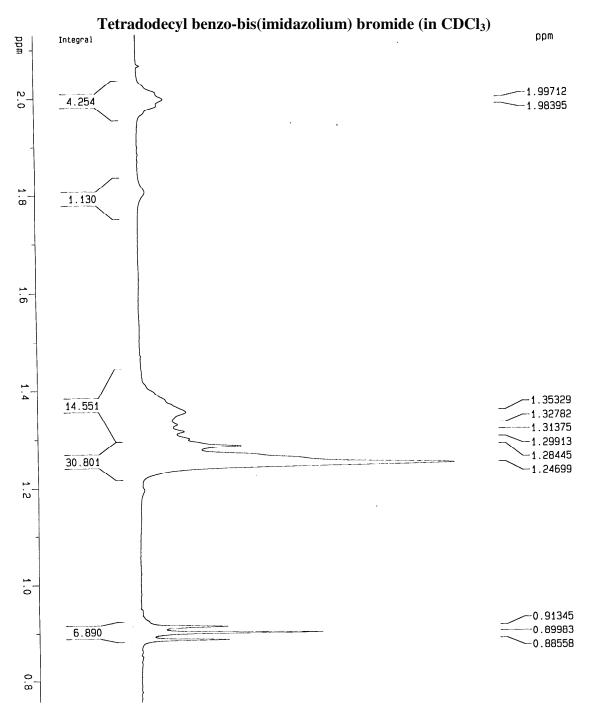




Tetradodecyl benzo-bis(imidazolium) bromide (in CDCl<sub>3</sub>)

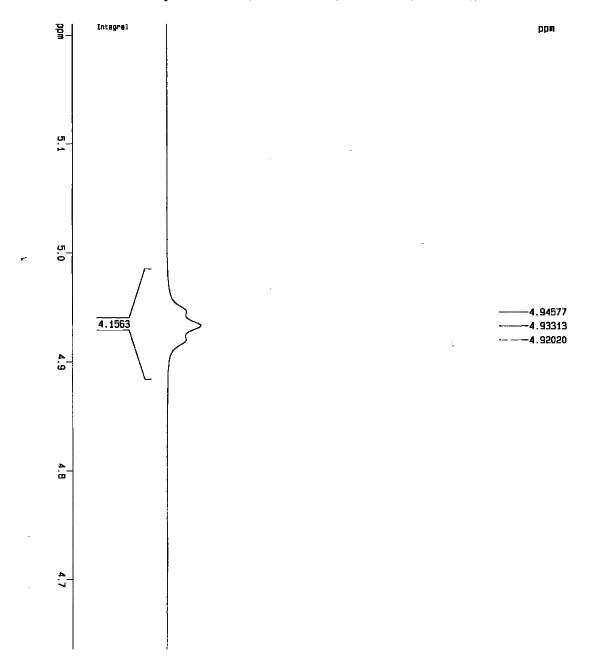


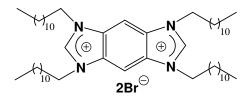




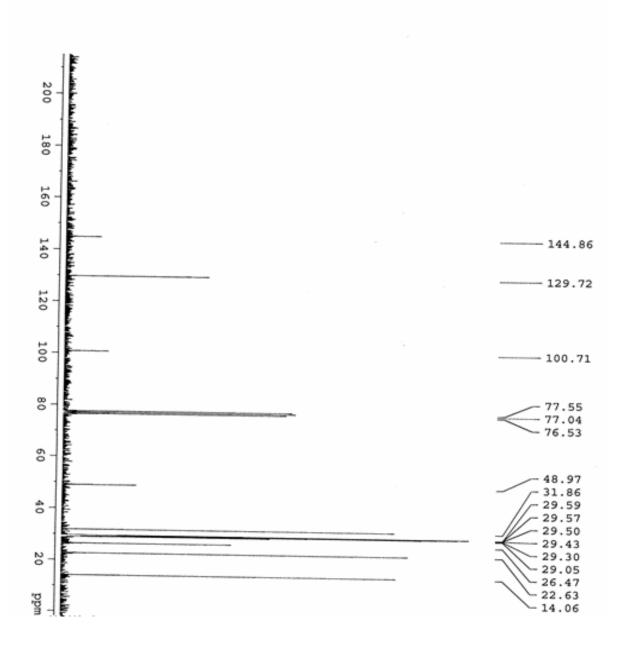


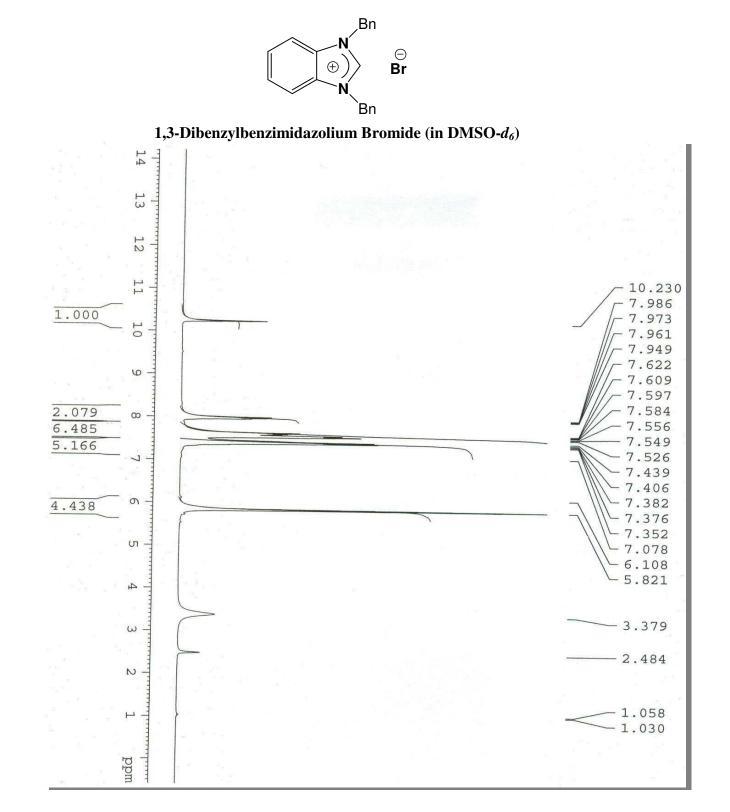
Tetradodecyl benzo-bis(imidazolium) bromide (in CDCl<sub>3</sub>)



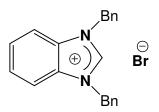


Tetradodecyl benzo-bis(imidazolium) bromide (in CDCl<sub>3</sub>)

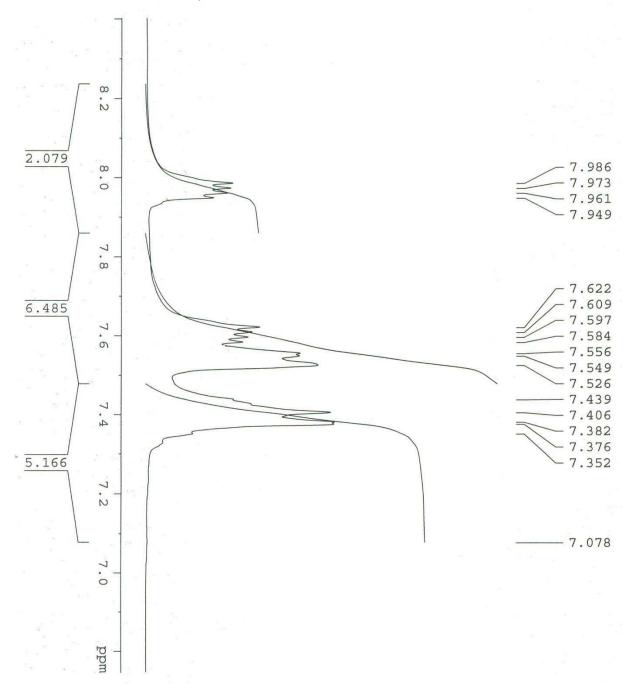


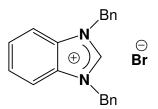


S27

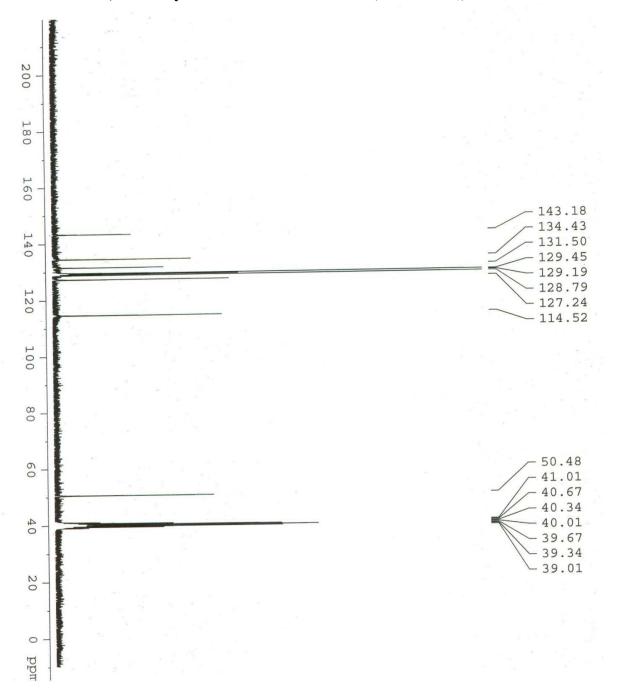


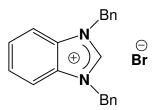
### 1,3-Dibenzylbenzimidazolium Bromide (in DMSO-d<sub>6</sub>)



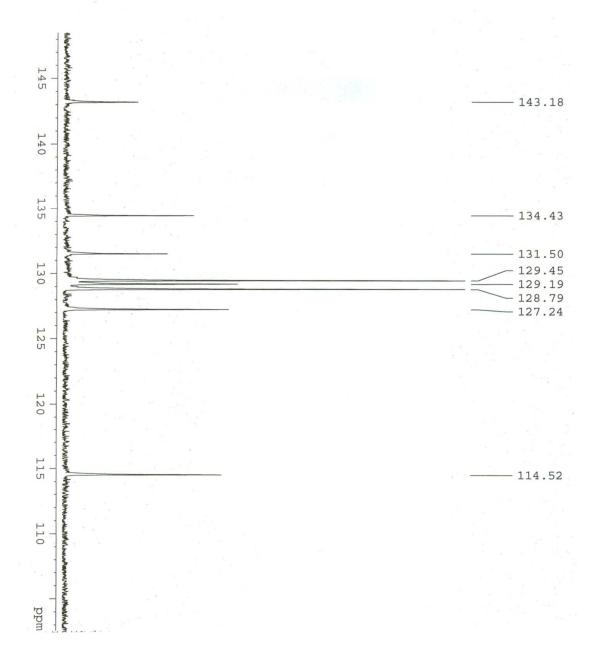


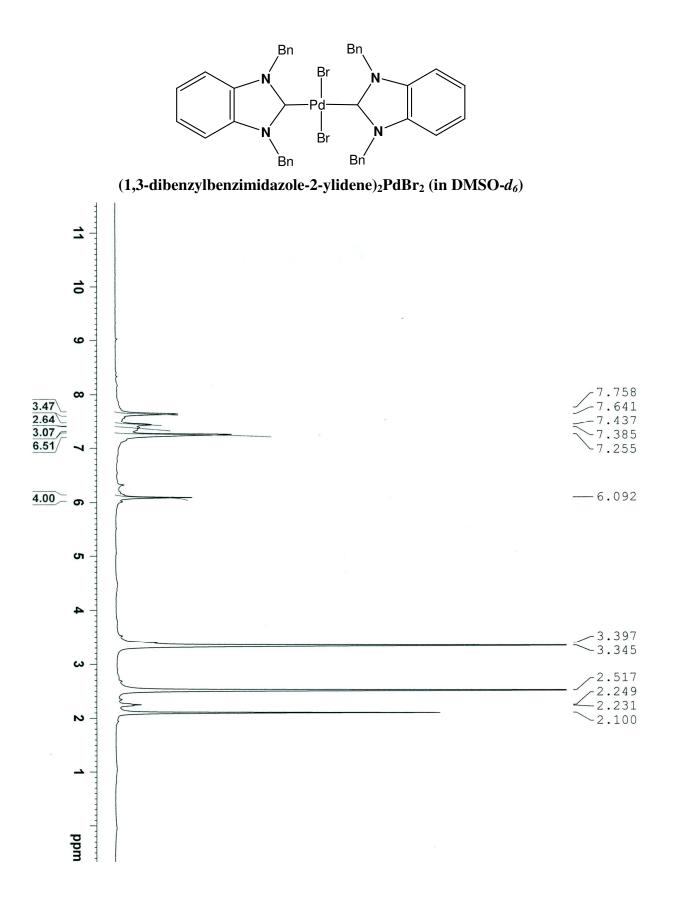
1,3-Dibenzylbenzimidazolium Bromide (in DMSO-d<sub>6</sub>)

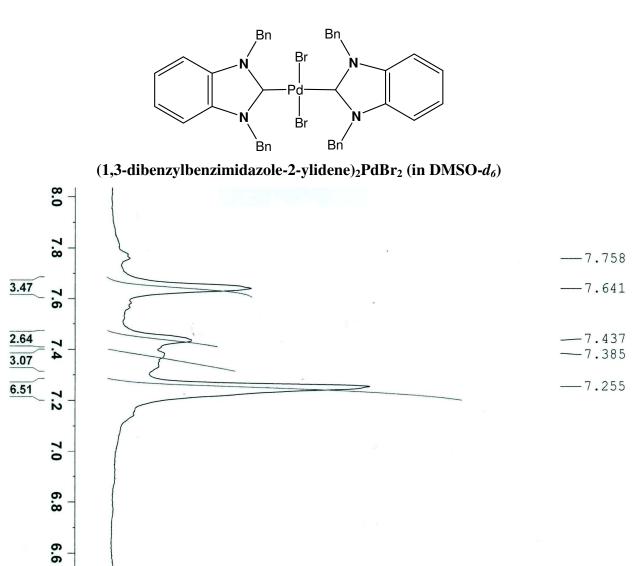




1,3-Dibenzylbenzimidazolium Bromide (in DMSO-*d*<sub>6</sub>)







6.4

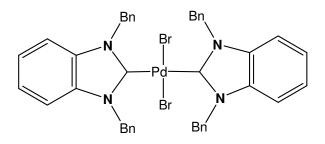
6.2

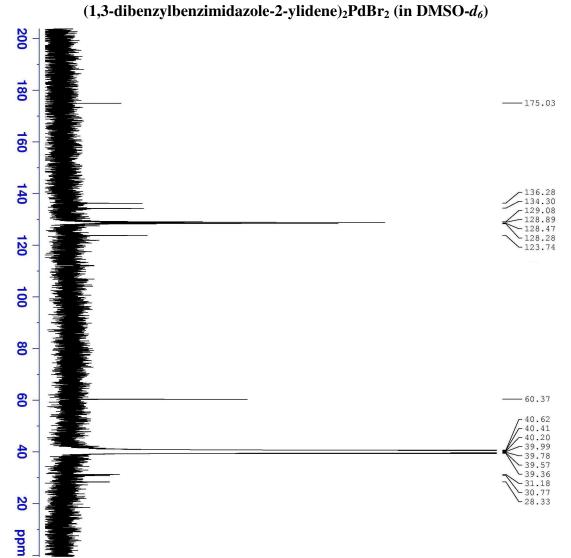
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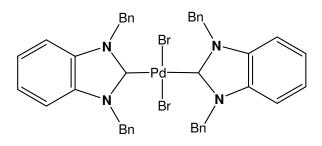
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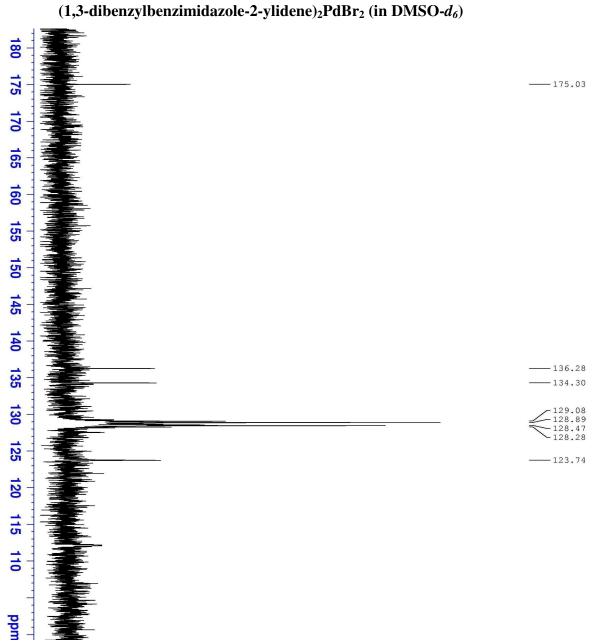
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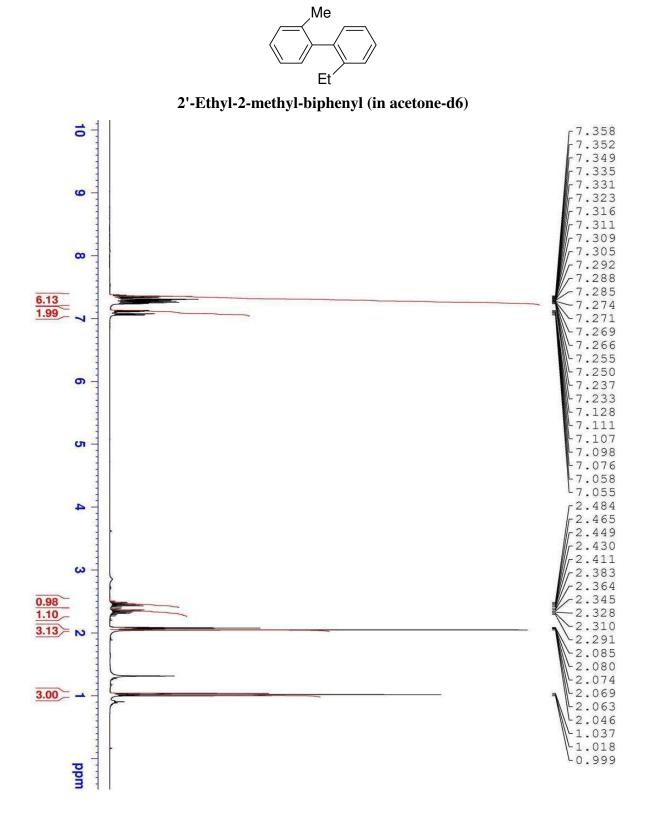
4.00

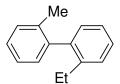




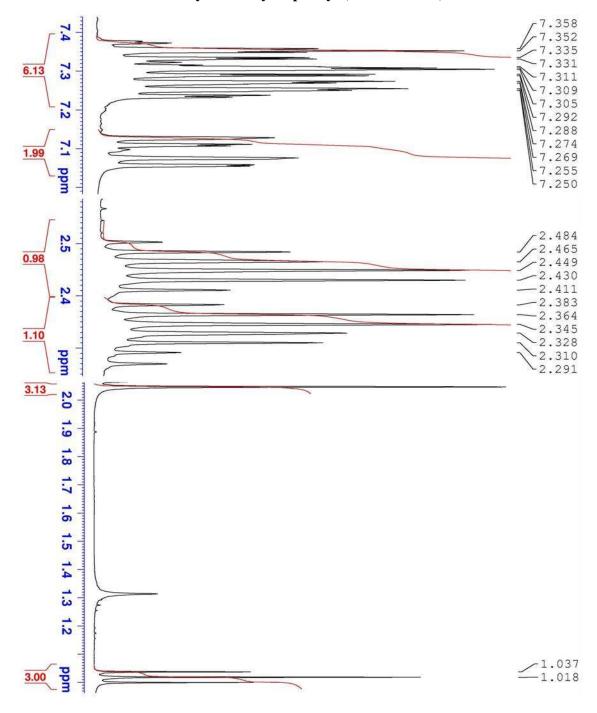


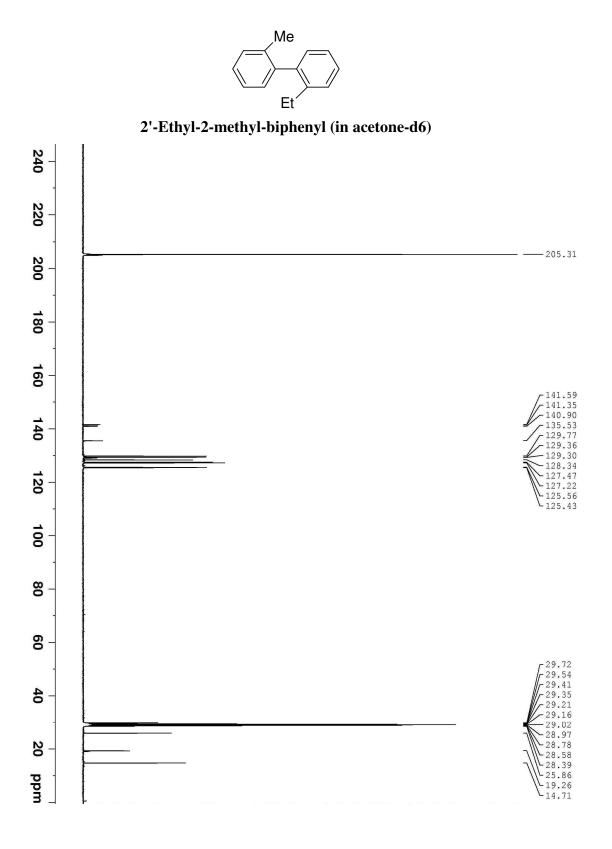


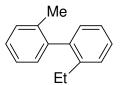




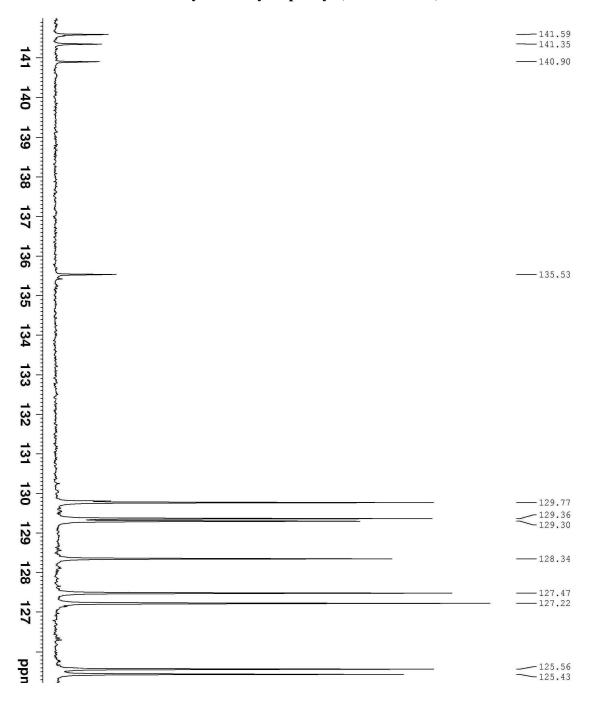
2'-Ethyl-2-methyl-biphenyl (in acetone-d6)

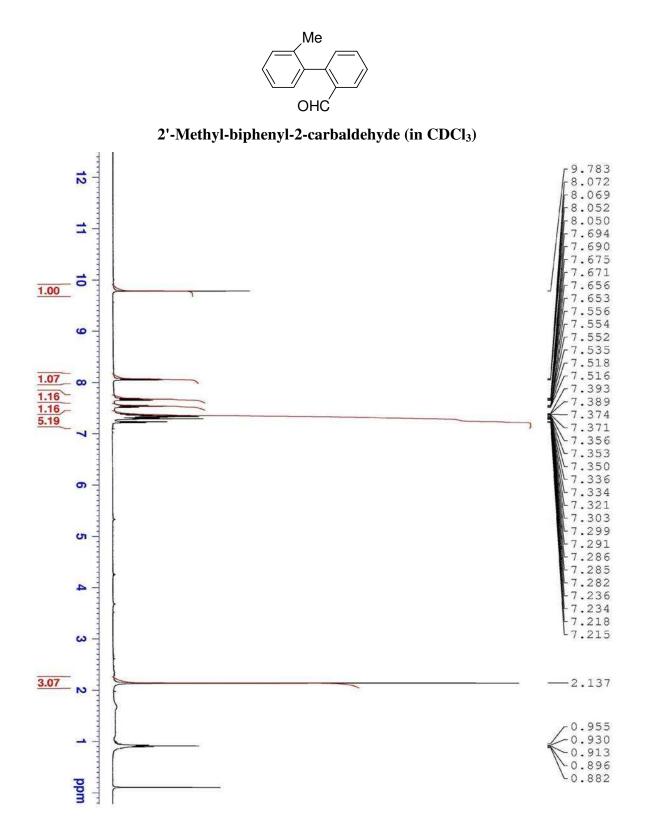


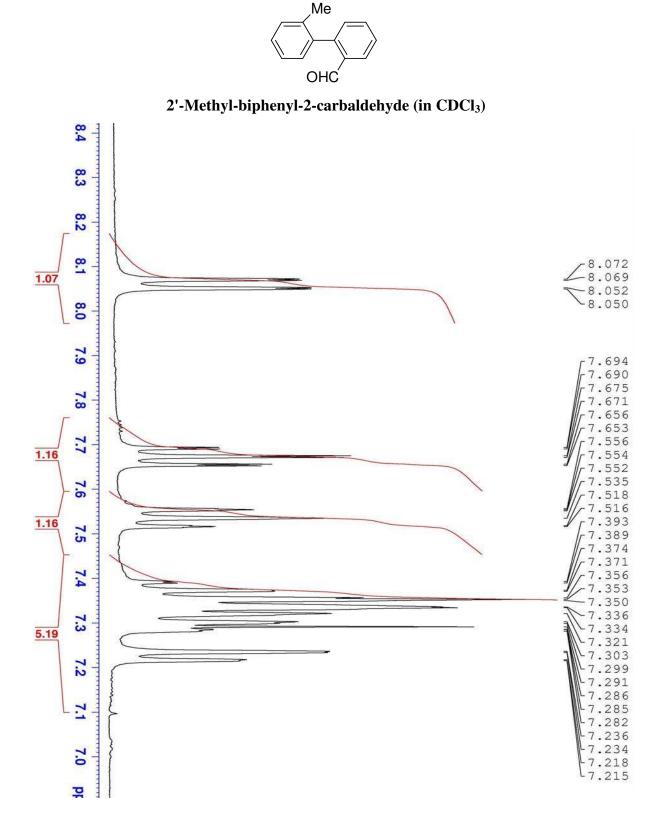


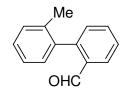


## 2'-Ethyl-2-methyl-biphenyl (in acetone-d6)

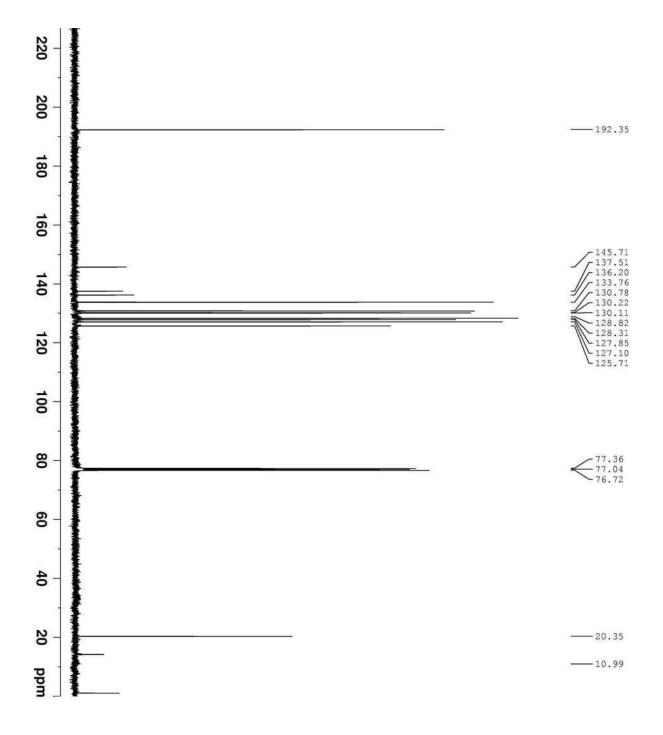


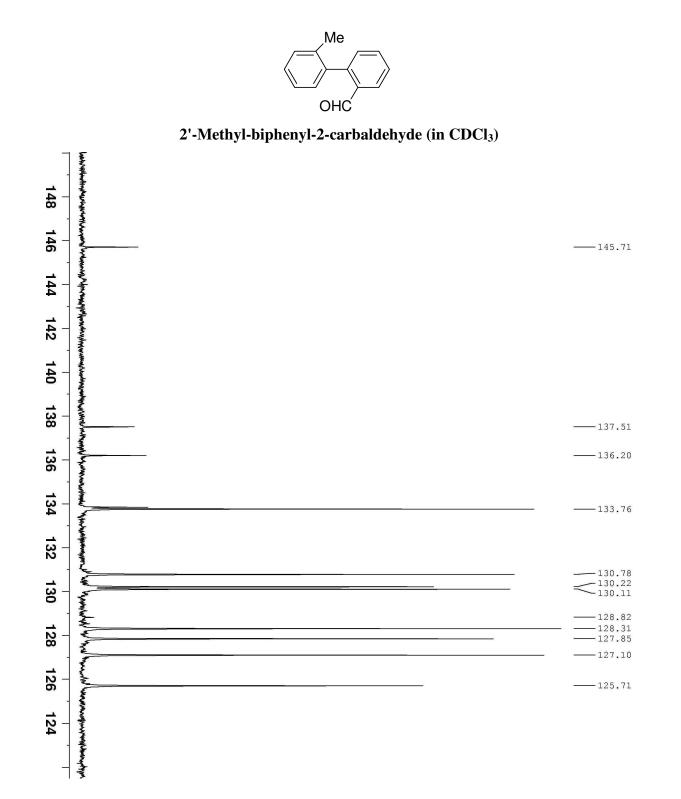




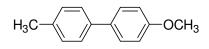


2'-Methyl-biphenyl-2-carbaldehyde (in CDCl<sub>3</sub>)

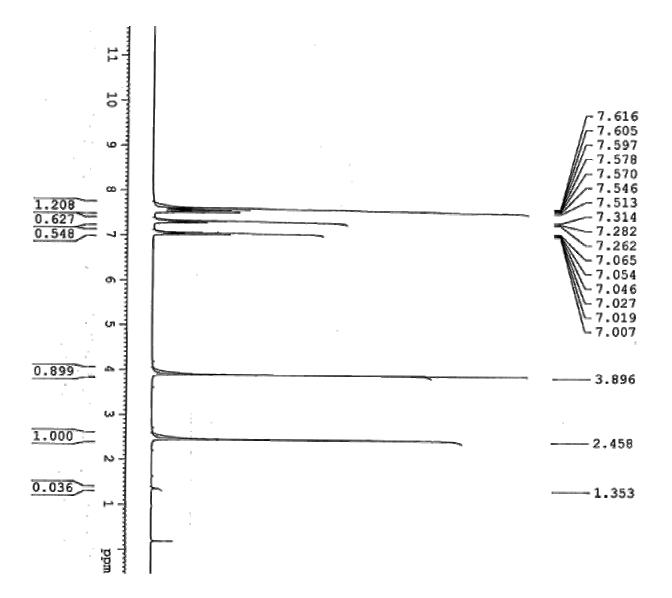


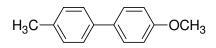


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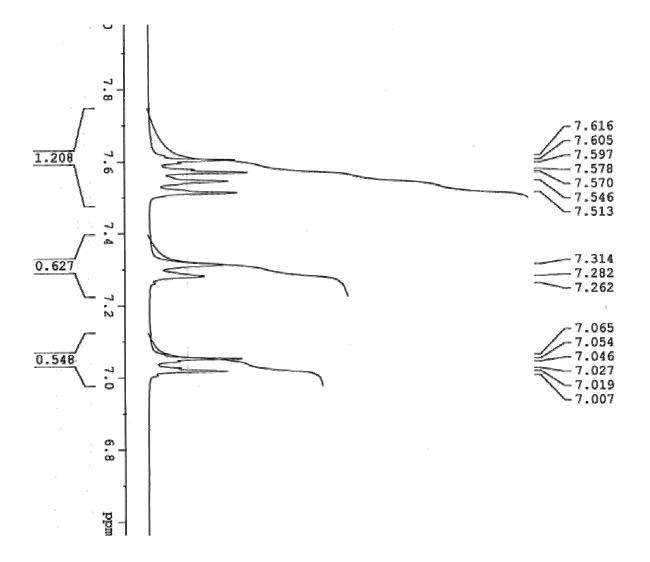


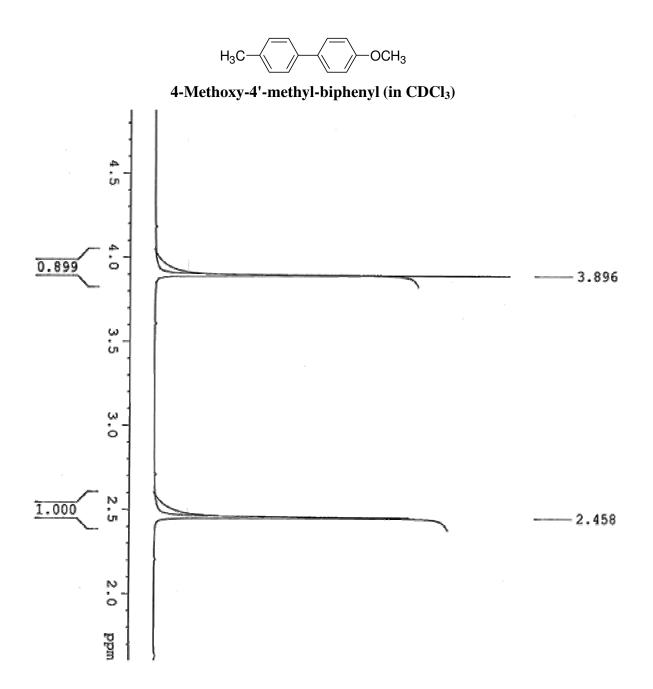
4-Methoxy-4'-methyl-biphenyl (in CDCl<sub>3</sub>)

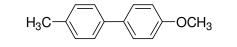




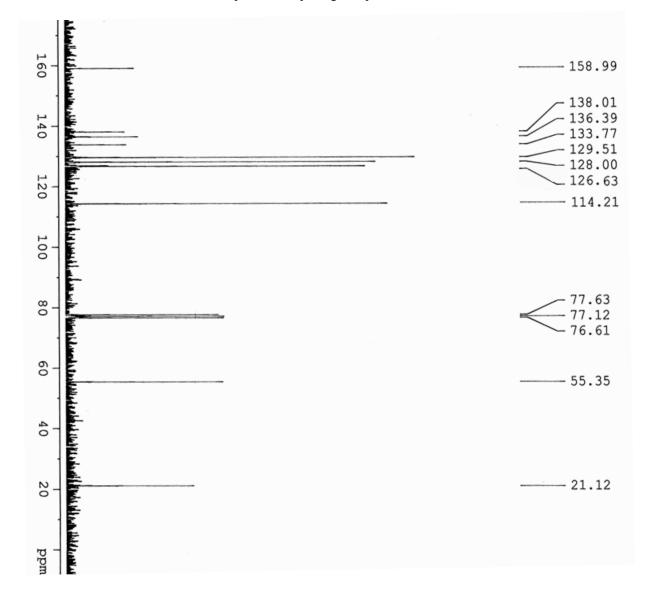
4-Methoxy-4'-methyl-biphenyl (in CDCl<sub>3</sub>)

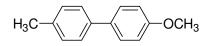




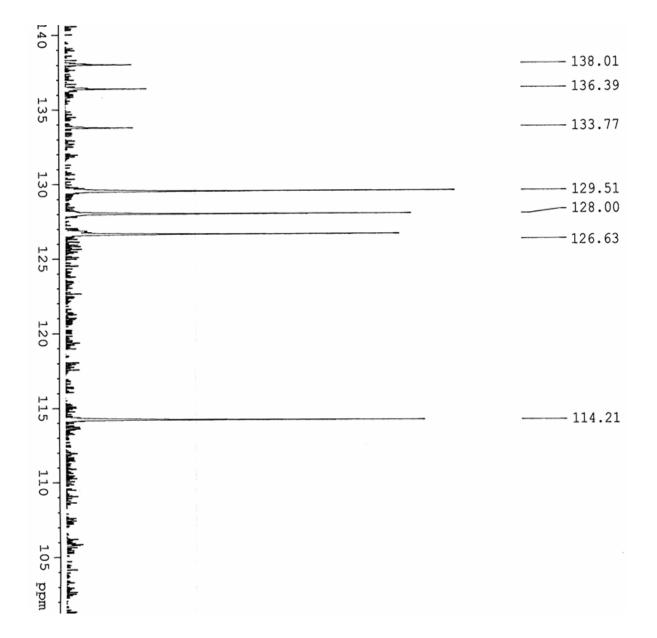


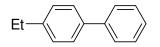
4-Methoxy-4'-methyl-biphenyl (in CDCl<sub>3</sub>)



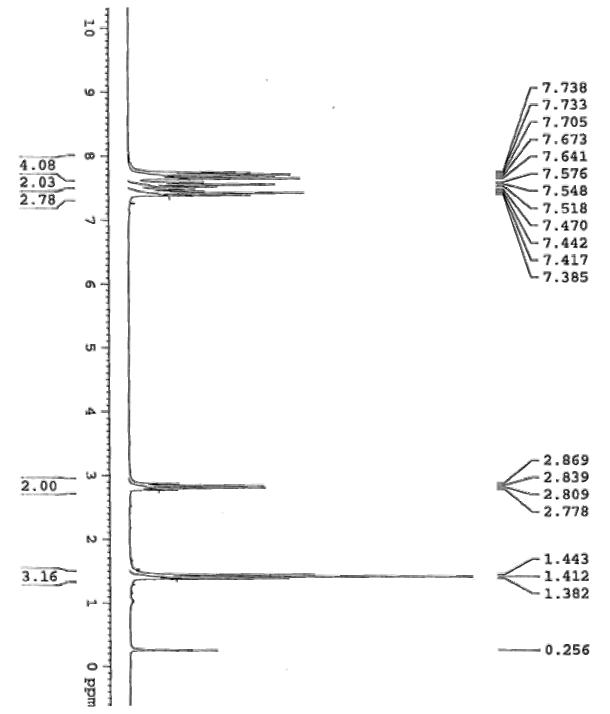


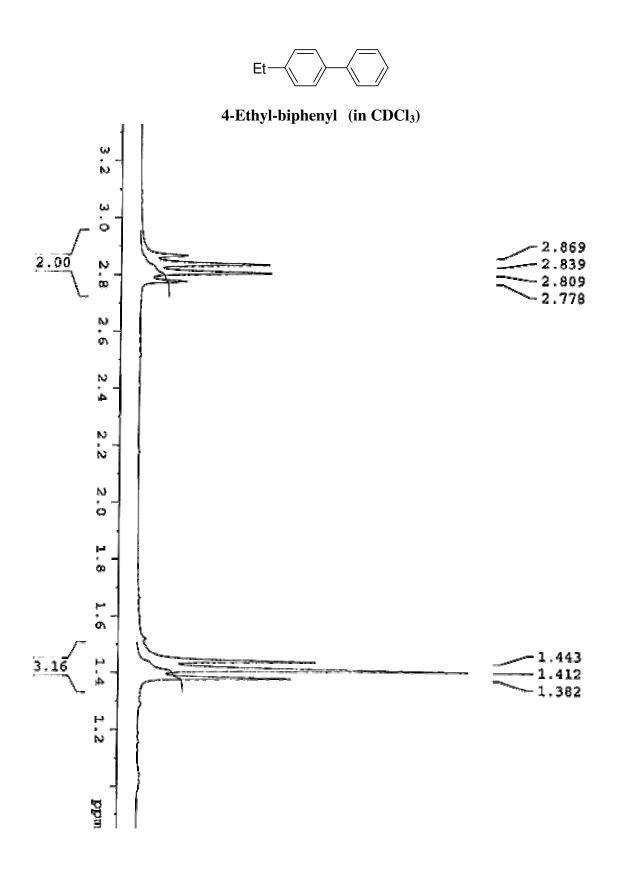
4-Methoxy-4'-methyl-biphenyl (in CDCl<sub>3</sub>)

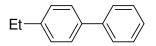




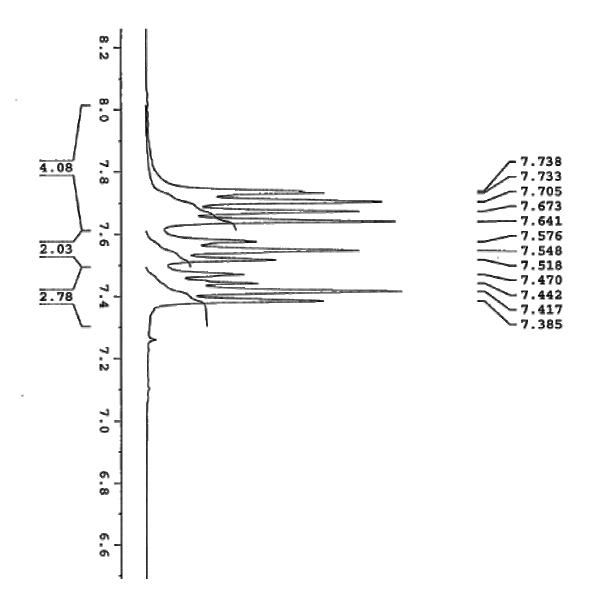


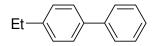




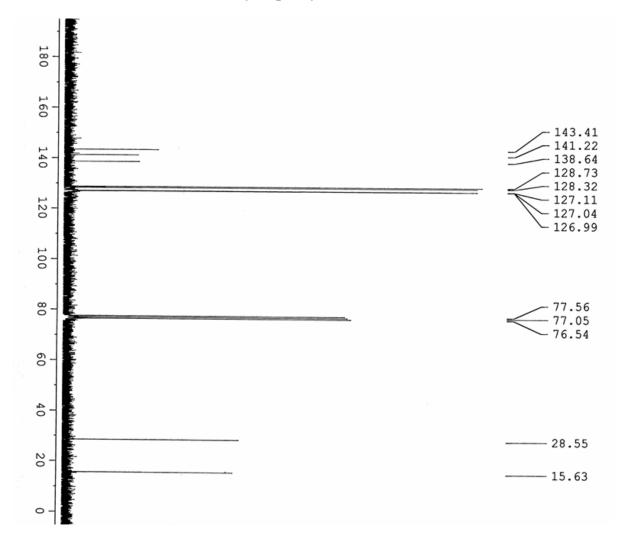


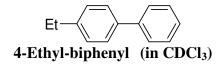
4-Ethyl-biphenyl (in CDCl<sub>3</sub>)

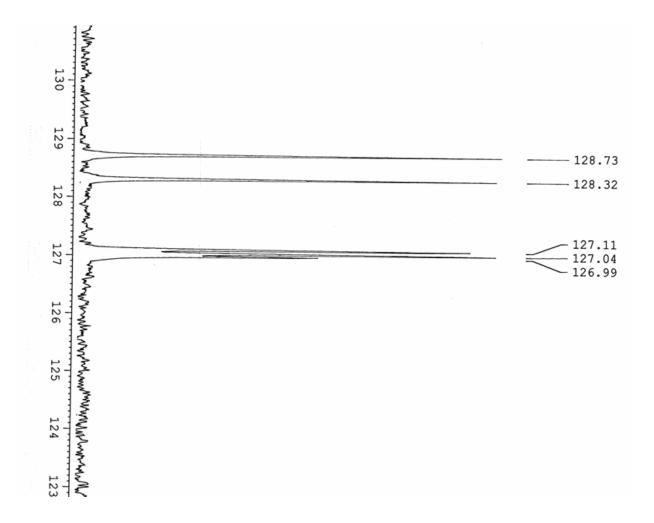


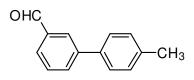


4-Ethyl-biphenyl (in CDCl<sub>3</sub>)

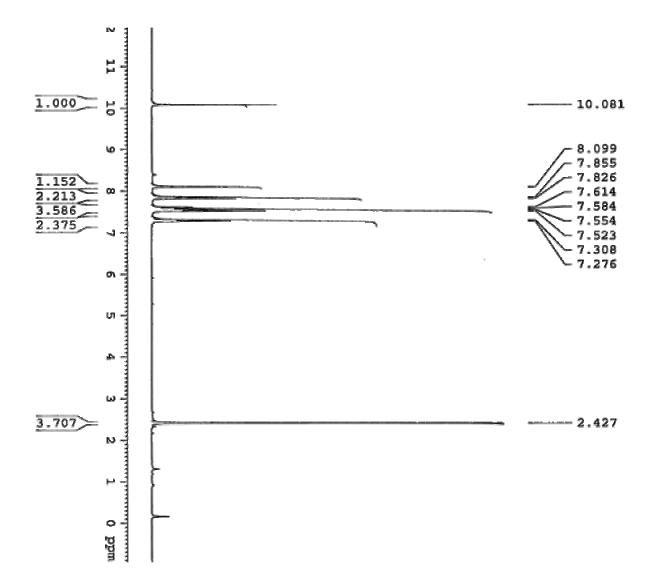


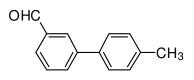




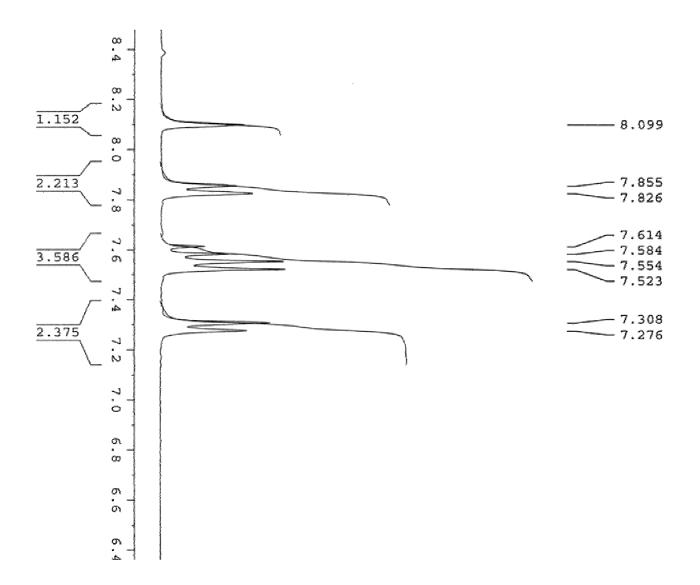


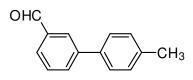
4'-methyl-biphenyl- 3-carbaldehyde (in CDCl<sub>3</sub>)

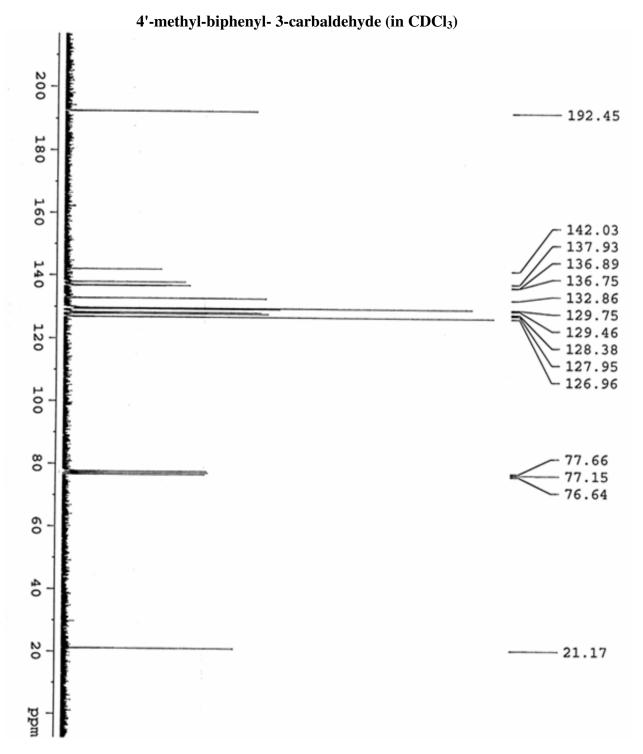


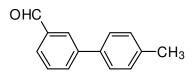


4'-methyl-biphenyl- 3-carbaldehyde (in CDCl<sub>3</sub>)

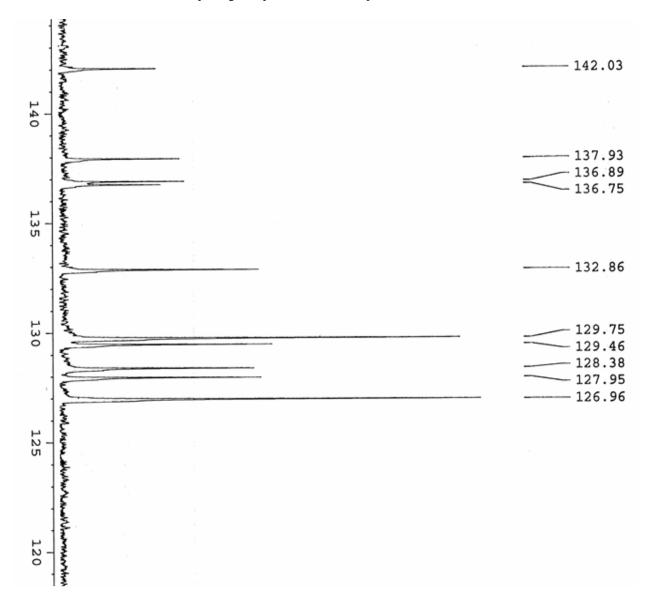


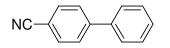




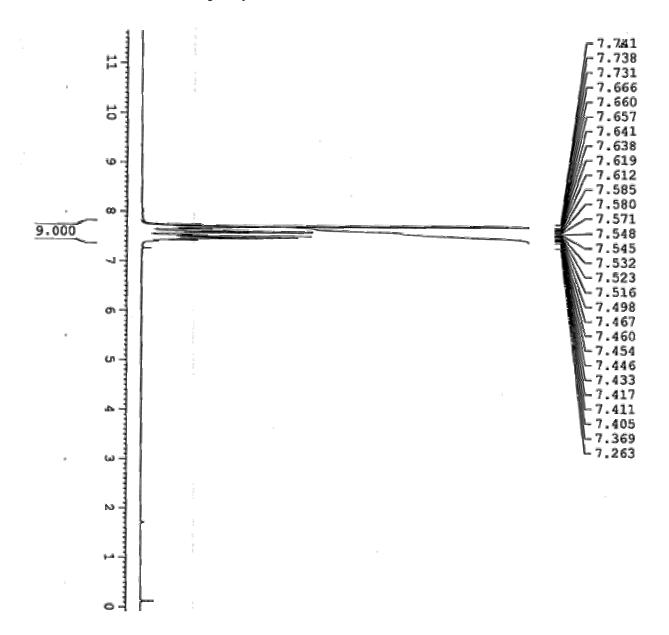


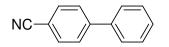
4'-methyl-biphenyl- 3-carbaldehyde (in CDCl<sub>3</sub>)



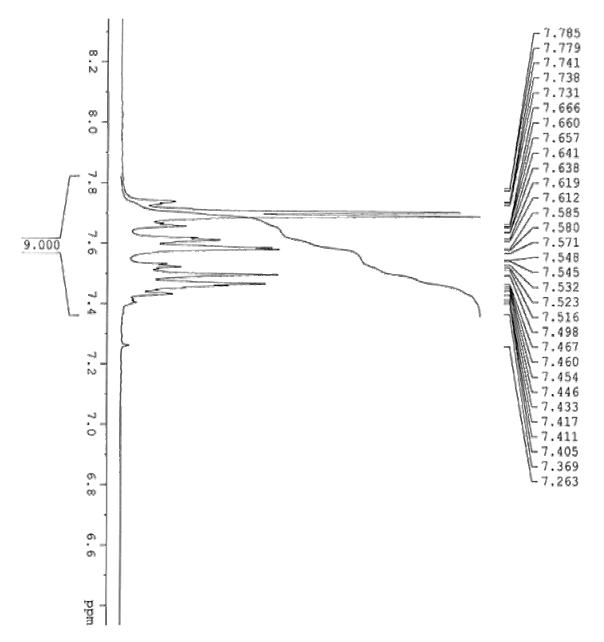


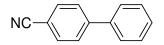
Biphenyl-4-carbonitrile (in CDCl<sub>3</sub>)



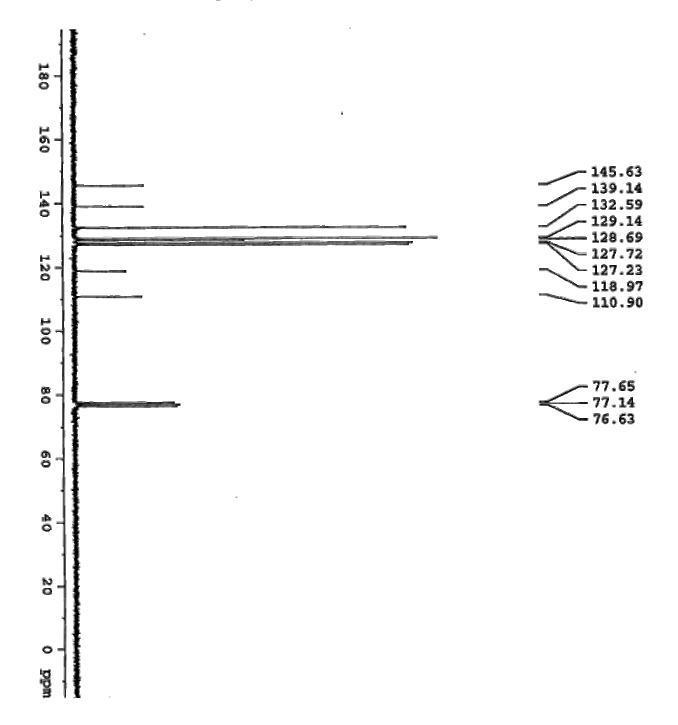


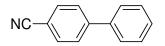




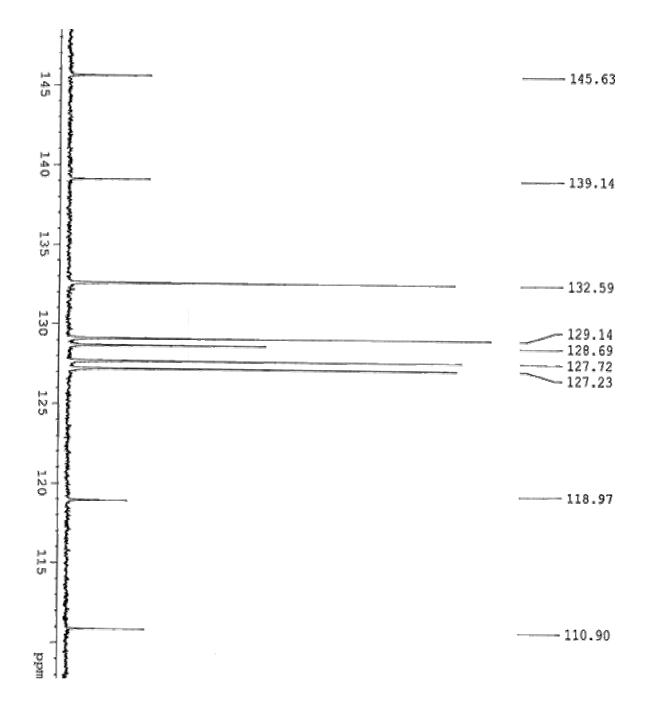


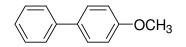




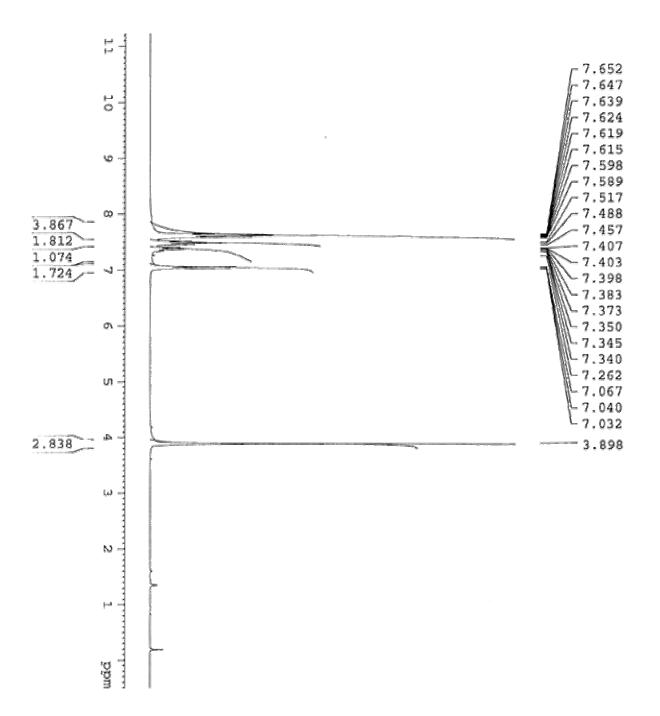


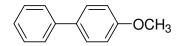
**Biphenyl-4-carbonitrile** (in CDCl<sub>3</sub>)



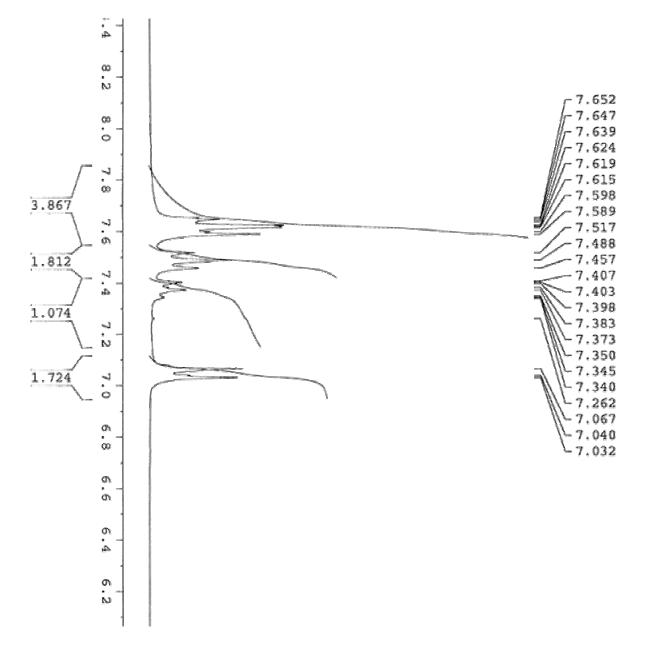


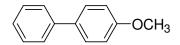
4-Methoxy-biphenyl (in CDCl<sub>3</sub>)



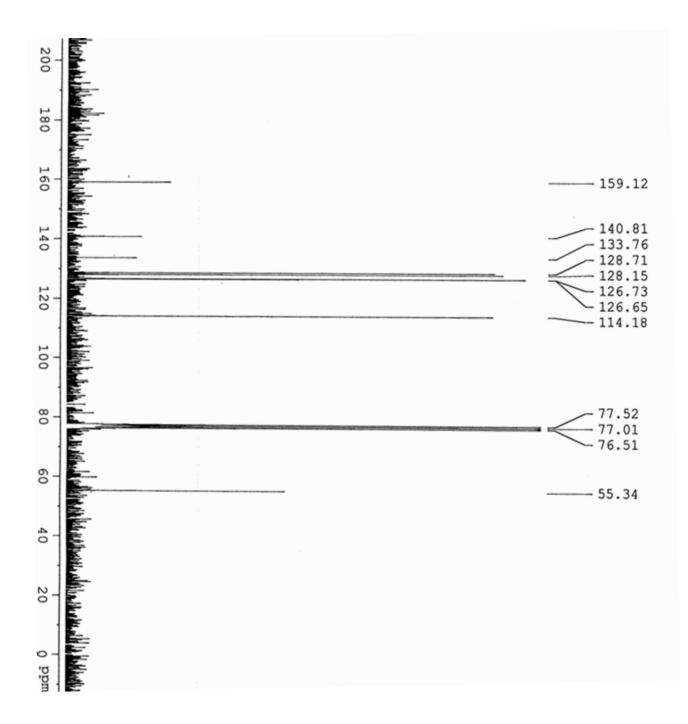


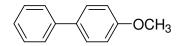
## 4-Methoxy-biphenyl (in CDCl<sub>3</sub>)



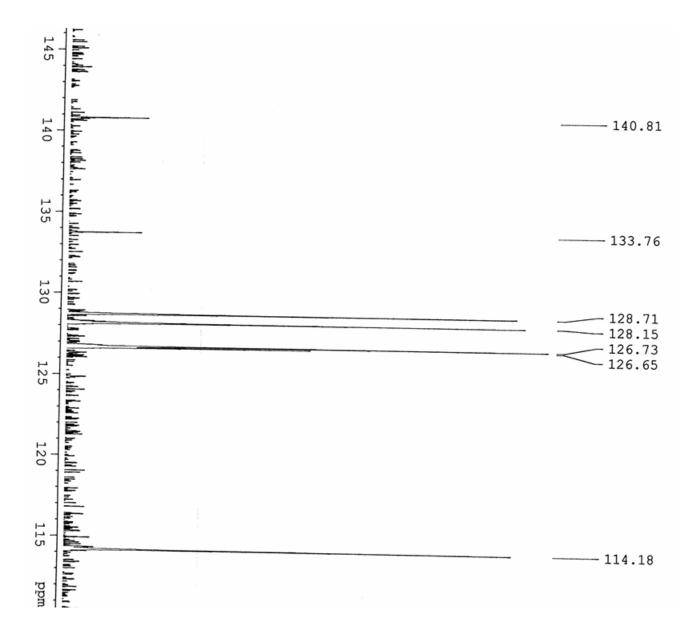


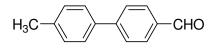
4-Methoxy-biphenyl (in CDCl<sub>3</sub>)



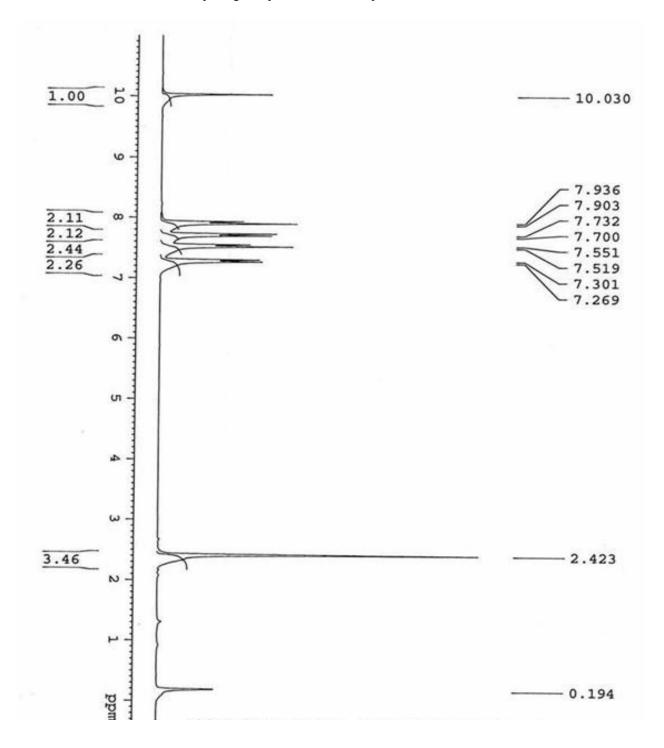


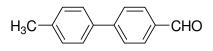
4-Methoxy-biphenyl (in CDCl<sub>3</sub>)



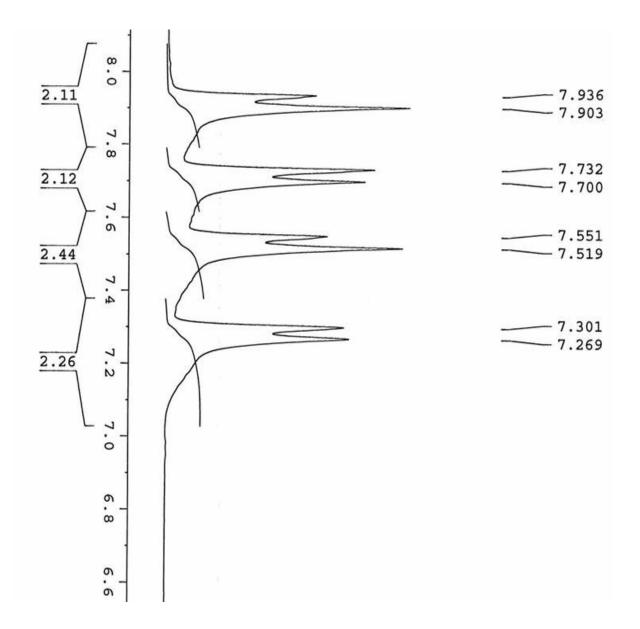


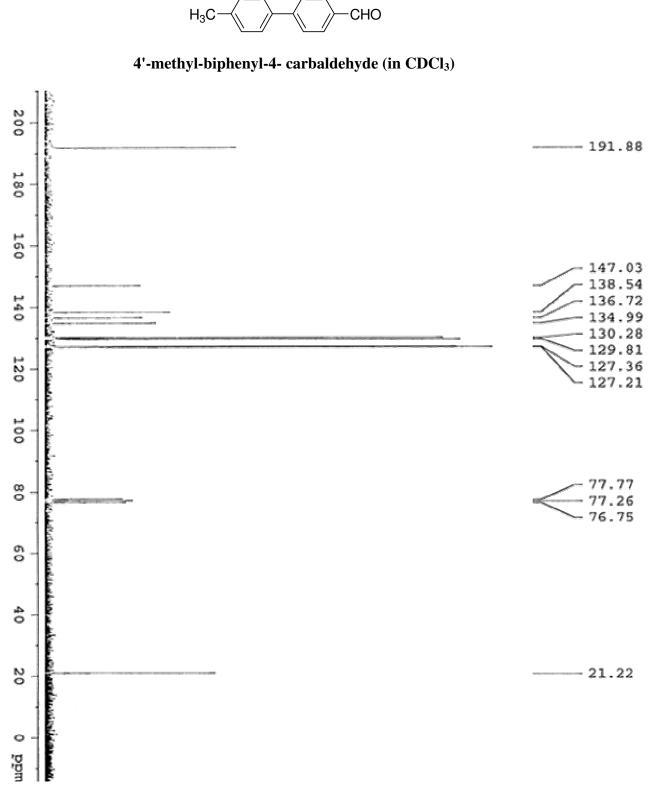
4'-methyl-biphenyl-4- carbaldehyde (in CDCl<sub>3</sub>)



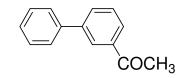


4'-methyl-biphenyl-4- carbaldehyde (in CDCl<sub>3</sub>)

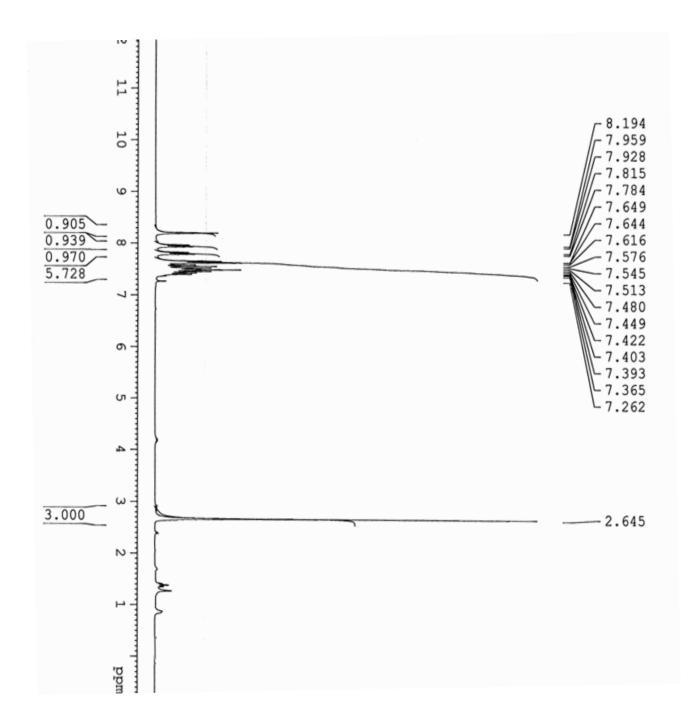


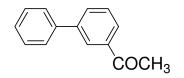


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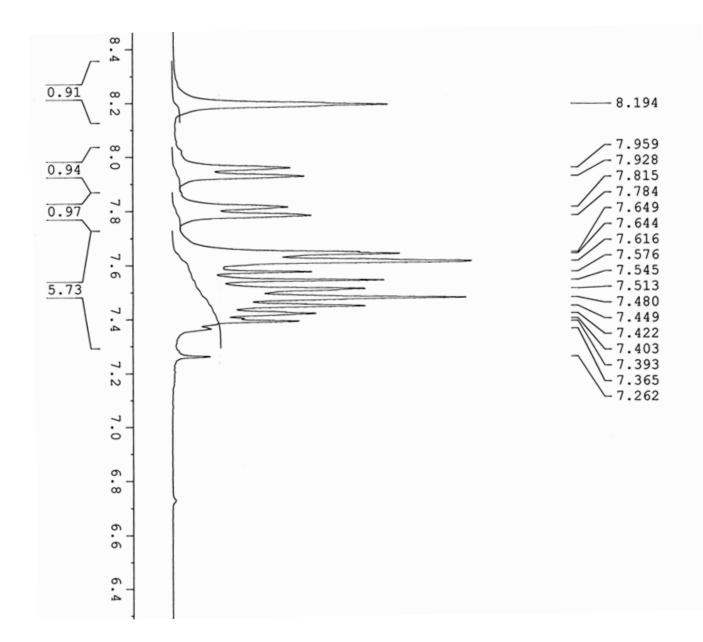


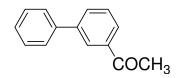
1-Biphenyl-3-yl-ethanone (in CDCl<sub>3</sub>)



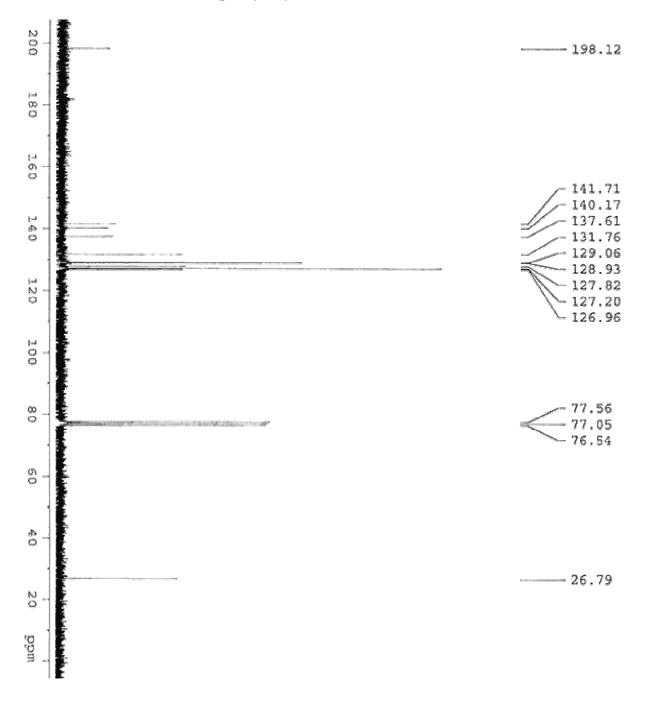


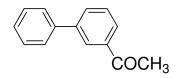
1-Biphenyl-3-yl-ethanone (in CDCl<sub>3</sub>)



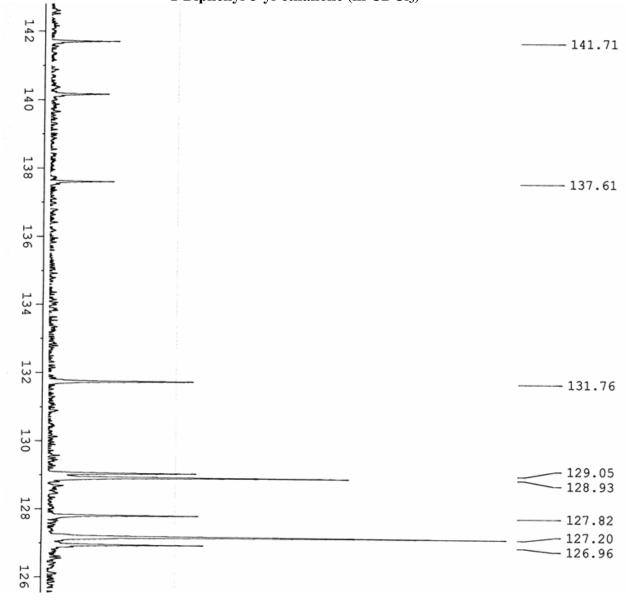


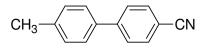
1-Biphenyl-3-yl-ethanone (in CDCl<sub>3</sub>)



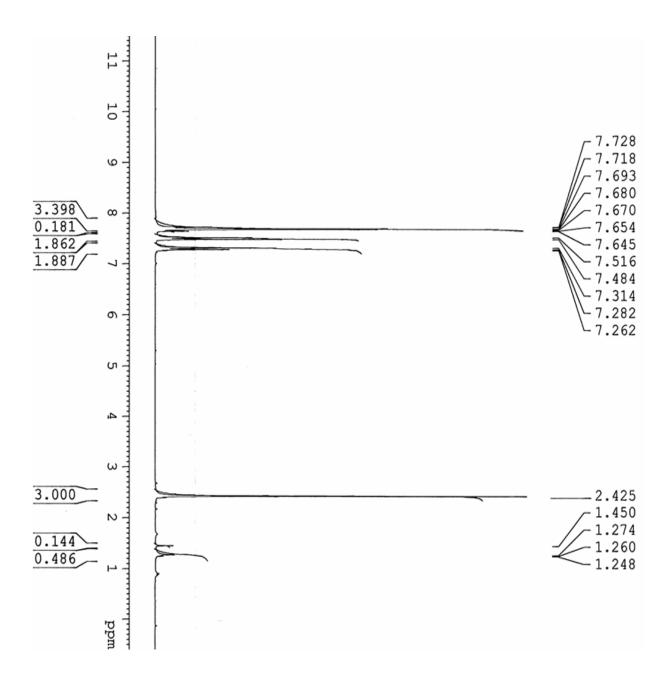


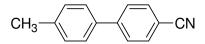
1-Biphenyl-3-yl-ethanone (in CDCl<sub>3</sub>)



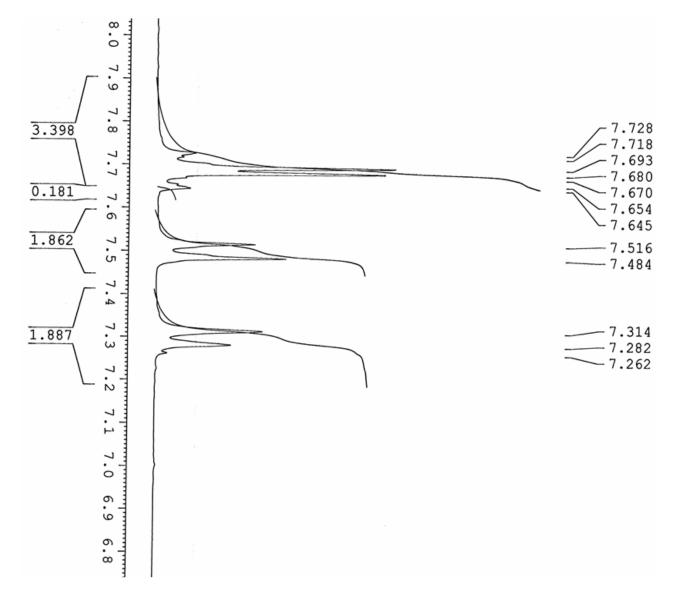


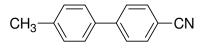
4'-Methyl-biphenyl-4-carbonitrile (in CDCl<sub>3</sub>)



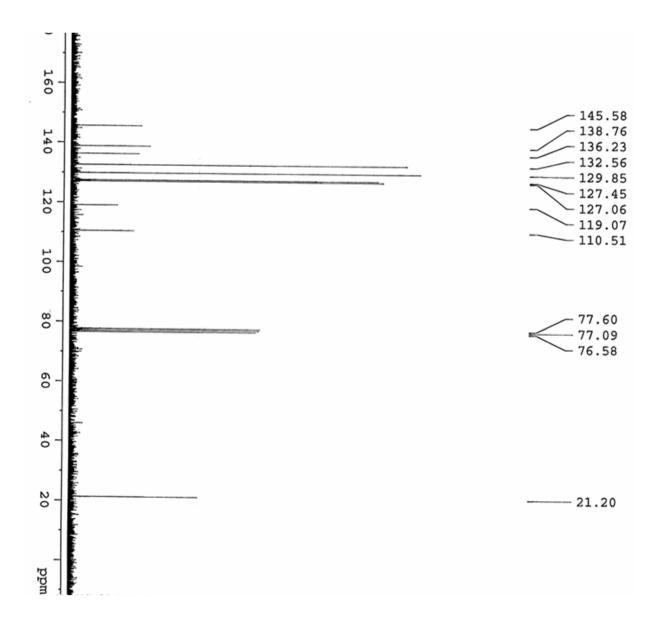


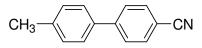
4'-Methyl-biphenyl-4-carbonitrile (in CDCl<sub>3</sub>)



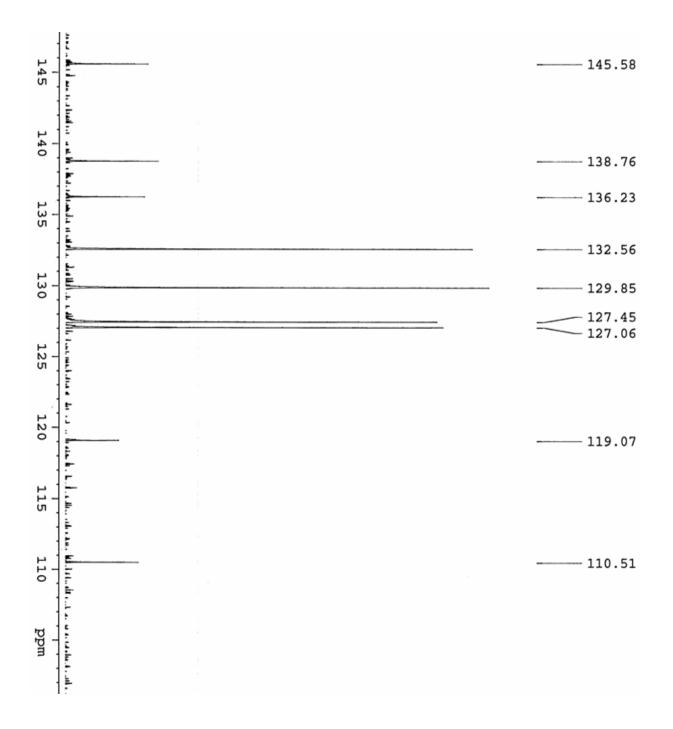


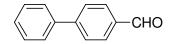
4'-Methyl-biphenyl-4-carbonitrile (in CDCl<sub>3</sub>)



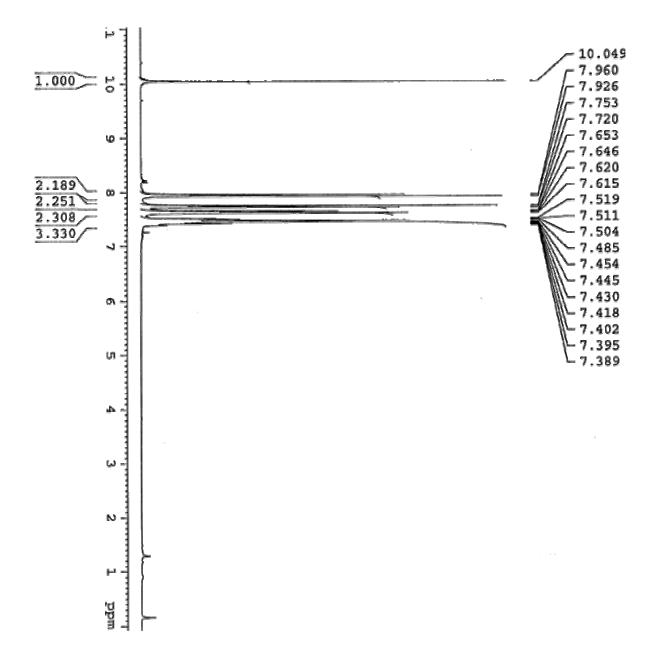


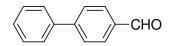
## 4'-Methyl-biphenyl-4-carbonitrile (in CDCl<sub>3</sub>)



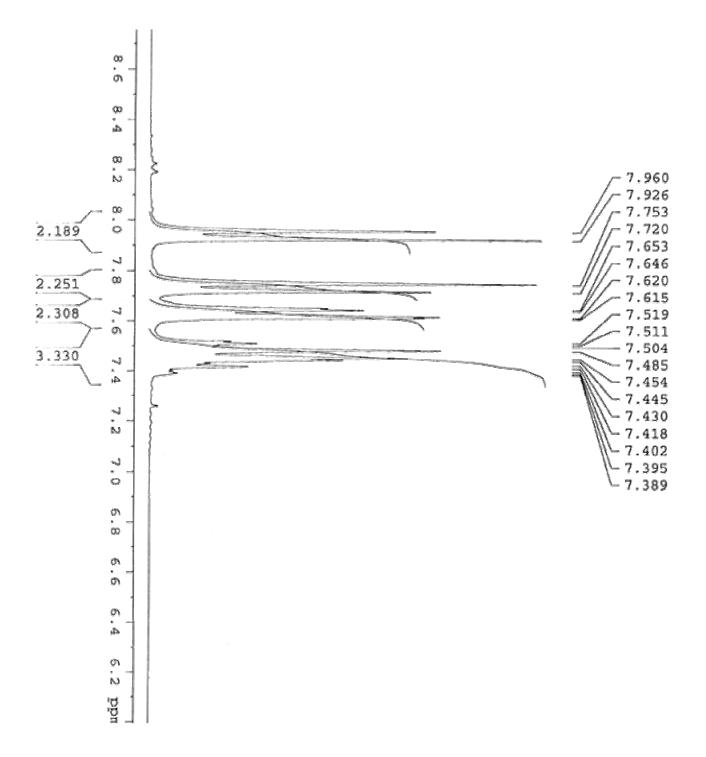


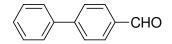
Phenyl- 4-carbaldehyde (in CDCl<sub>3</sub>)



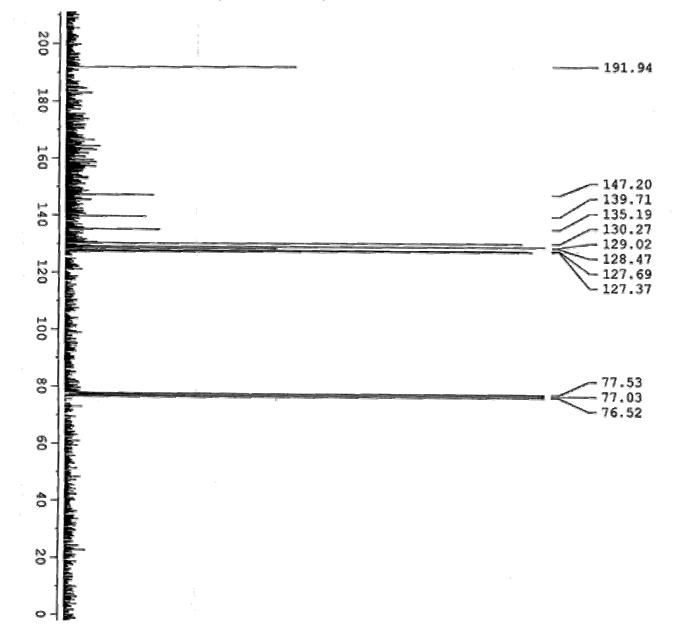


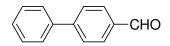




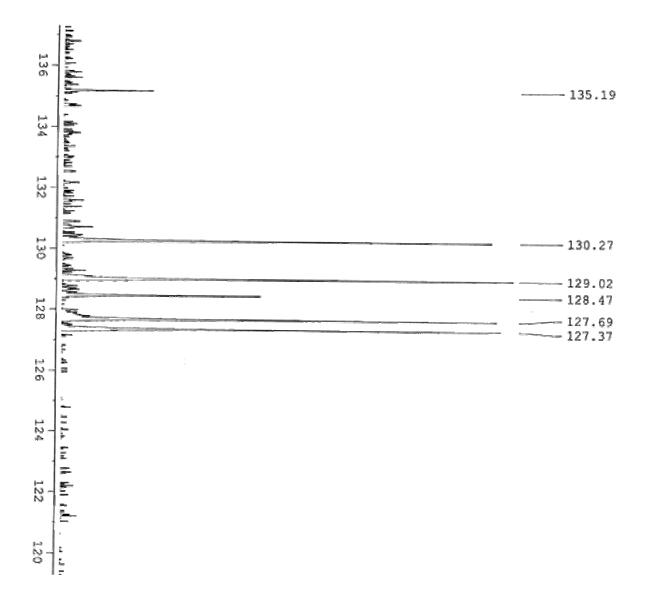


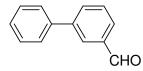
Phenyl- 4-carbaldehyde (in CDCl<sub>3</sub>)



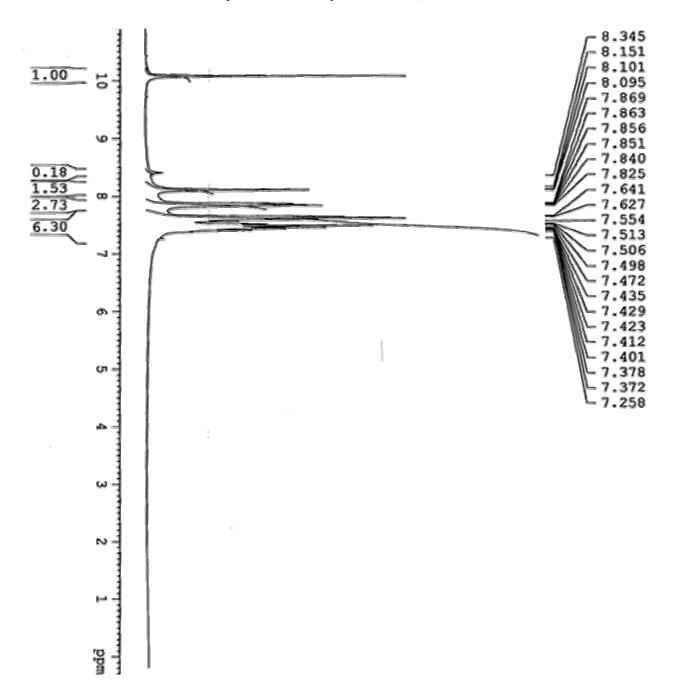


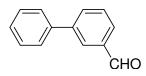
Phenyl- 4-carbaldehyde (in CDCl<sub>3</sub>)



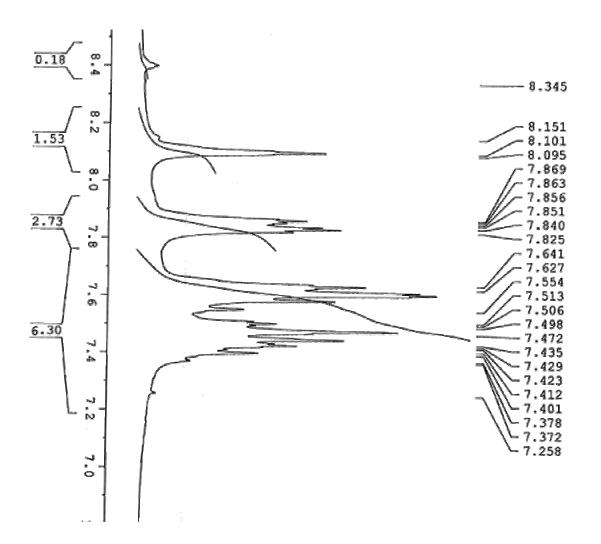


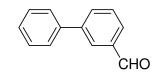




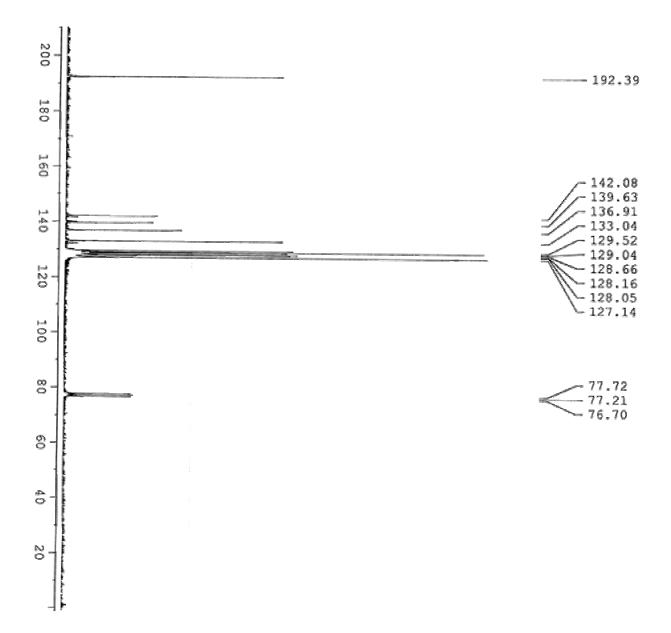


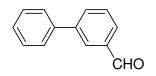
Phenyl- 4-carbaldehyde (in CDCl<sub>3</sub>)



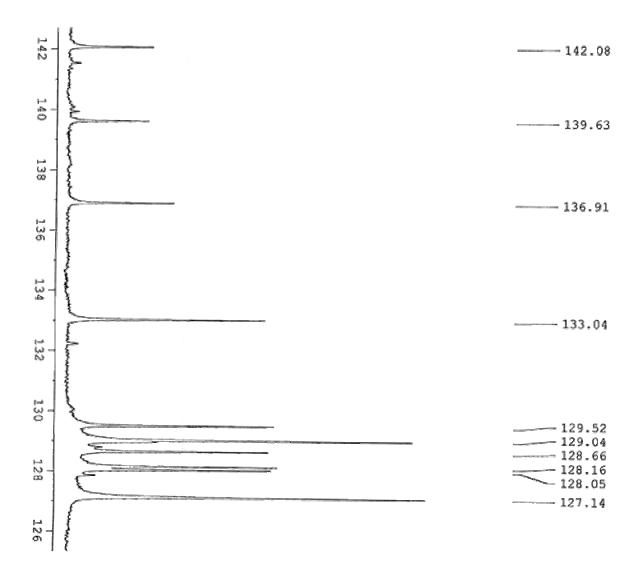


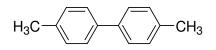




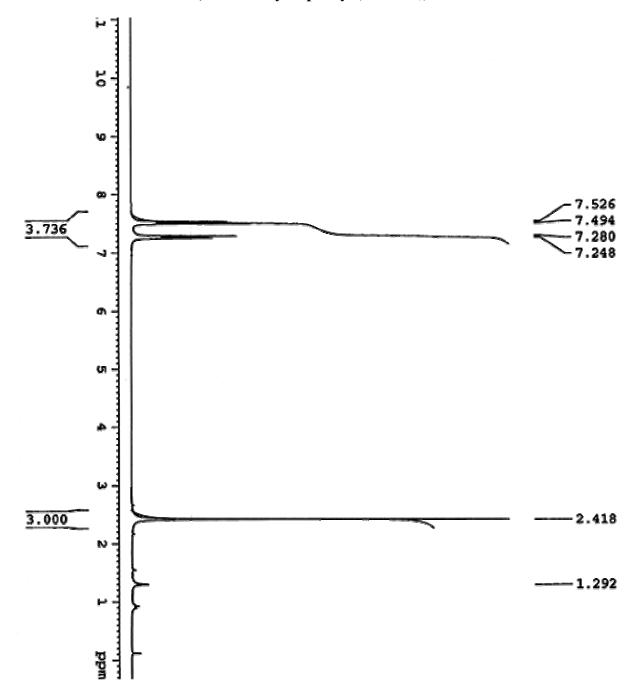


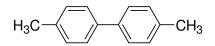




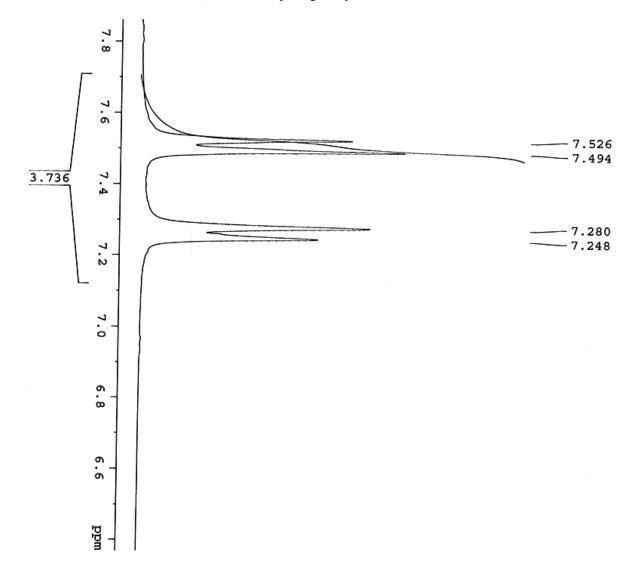


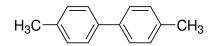
4, 4'-Dimethyl-biphenyl (in CDCl<sub>3</sub>)



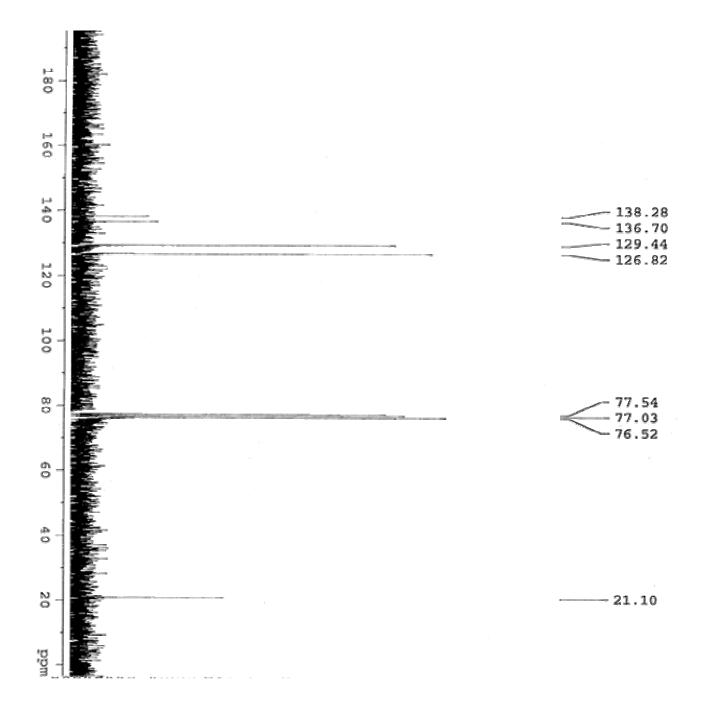


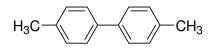
## 4, 4'-Dimethyl-biphenyl (in CDCl<sub>3</sub>)



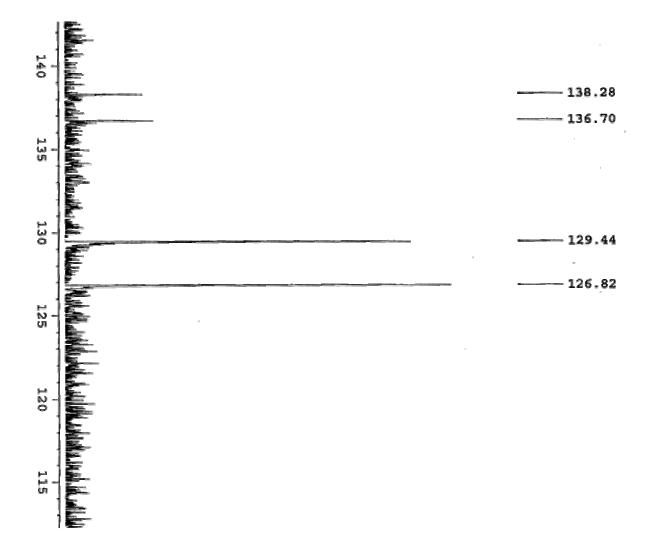


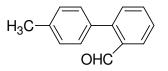
4, 4'-Dimethyl-biphenyl (in CDCl<sub>3</sub>)



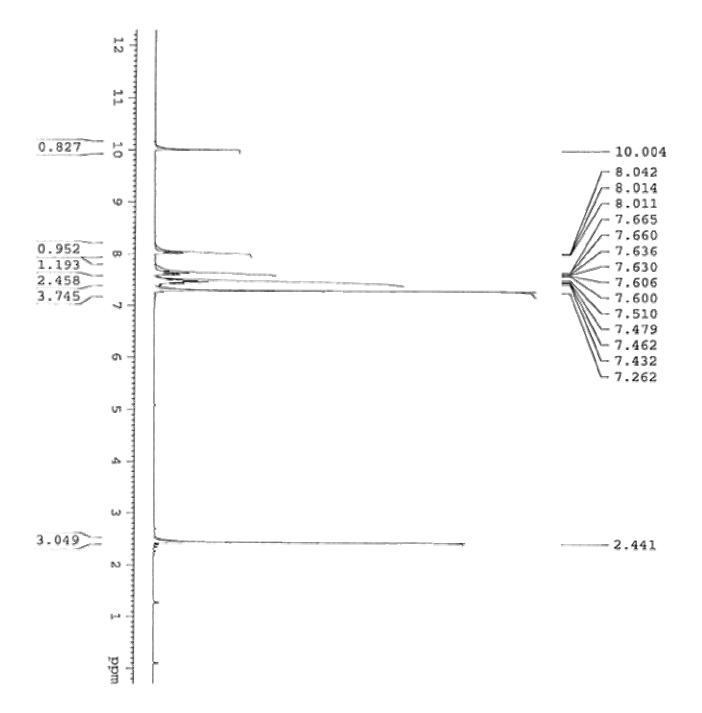


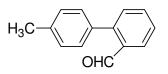
## 4, 4'-Dimethyl-biphenyl (in CDCl<sub>3</sub>)



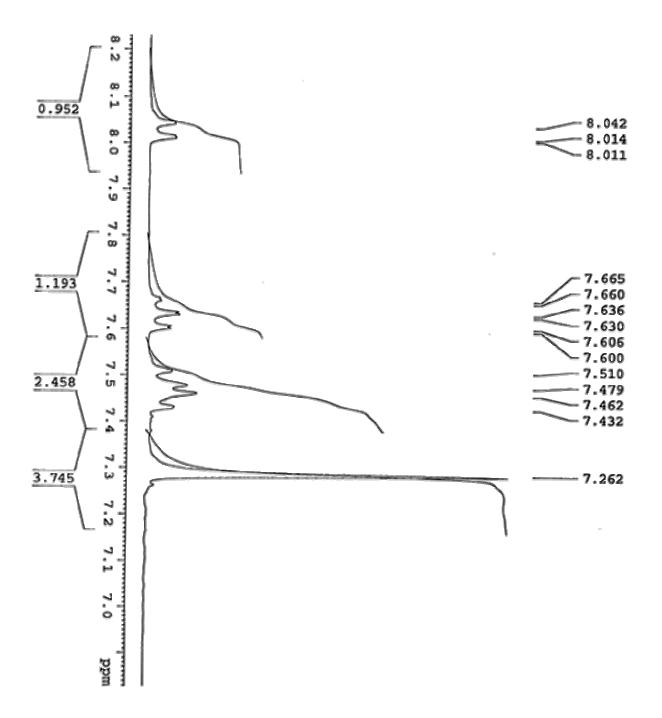


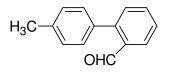
4'-Methyl-biphenyl-2-carbaldehyde (in CDCl<sub>3</sub>)



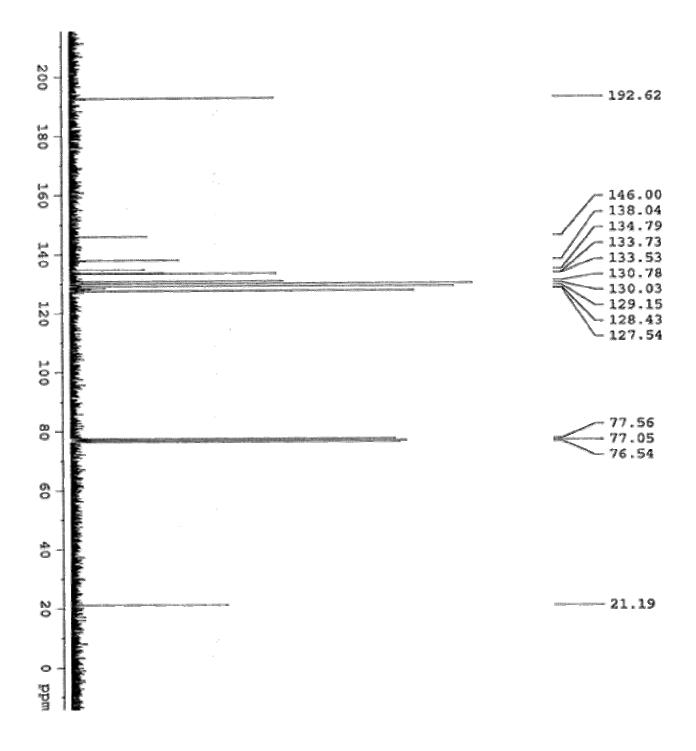


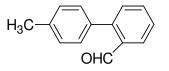
4'-Methyl-biphenyl-2-carbaldehyde (in CDCl<sub>3</sub>)

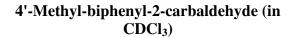


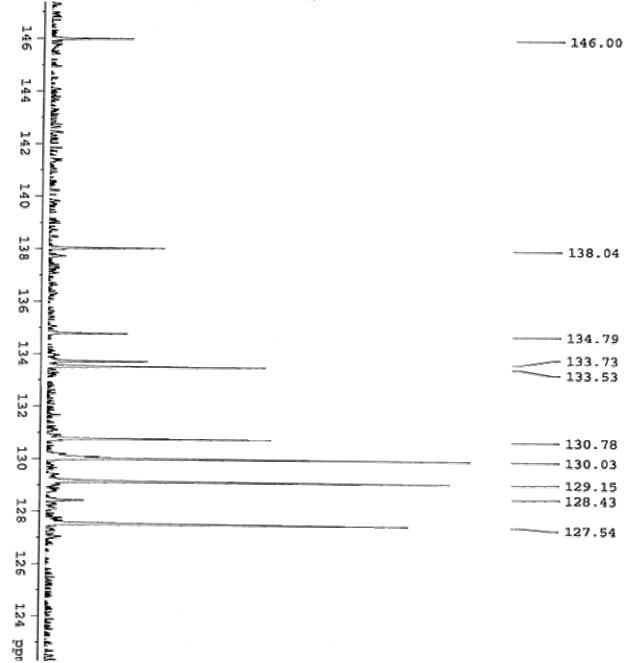


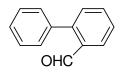
4'-Methyl-biphenyl-2-carbaldehyde (in CDCl<sub>3</sub>)



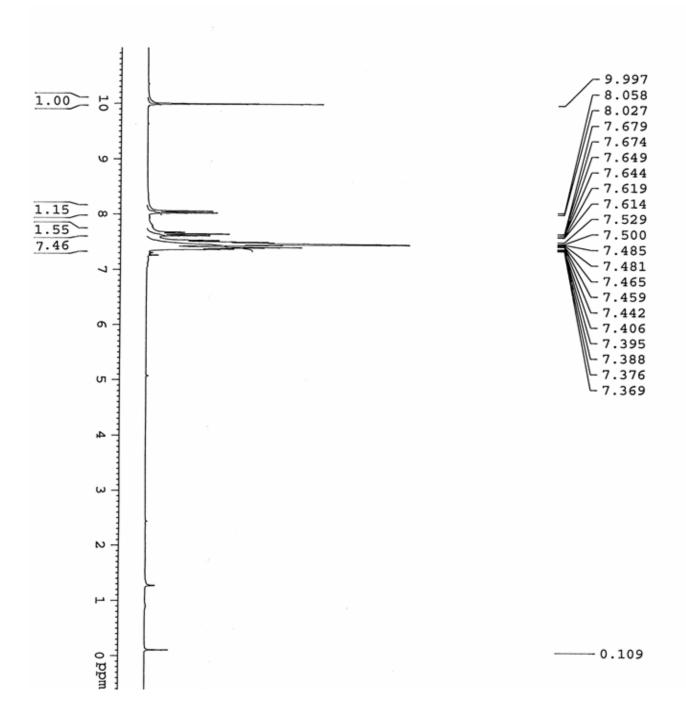


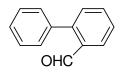




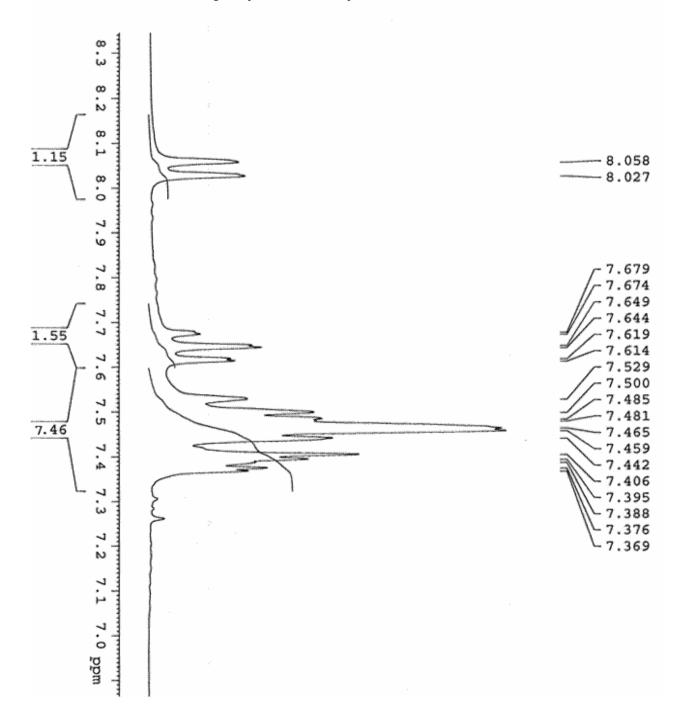


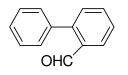
Biphenyl-2-carbaldehyde (in CDCl<sub>3</sub>)



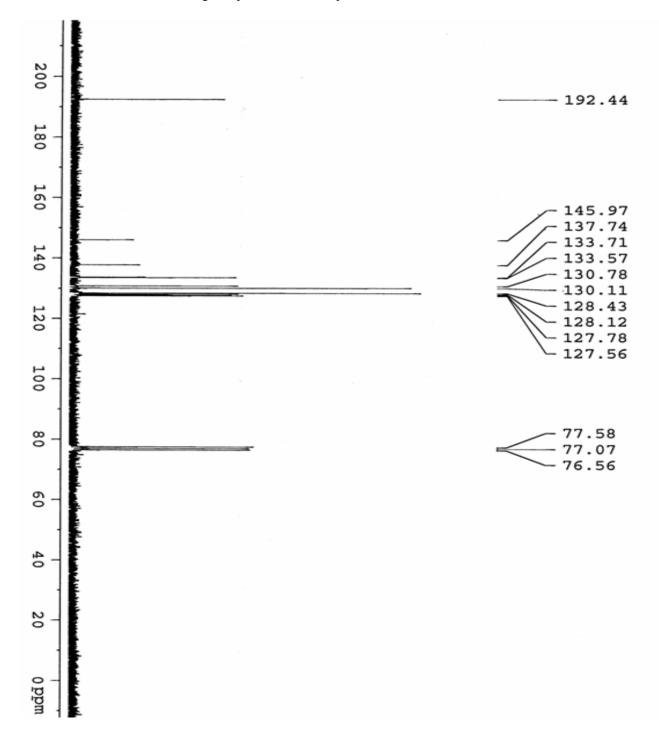


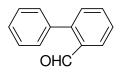
Biphenyl-2-carbaldehyde (in CDCl<sub>3</sub>)



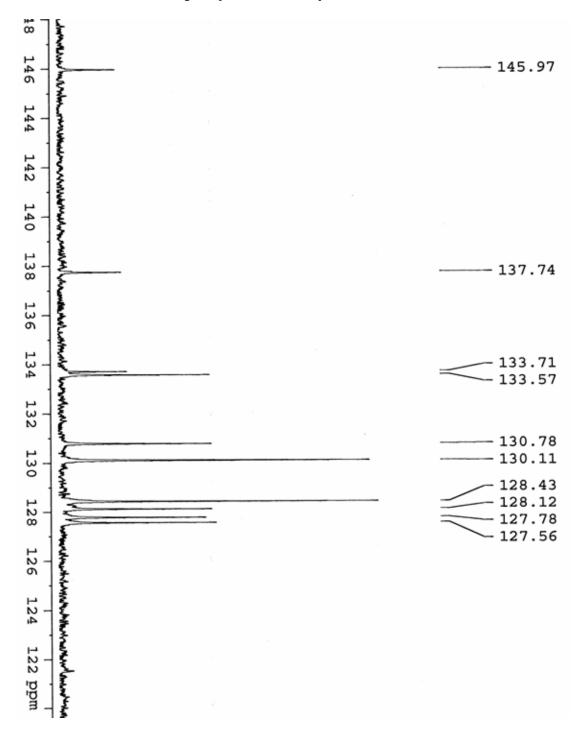


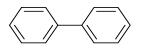
Biphenyl-2-carbaldehyde (in CDCl<sub>3</sub>)



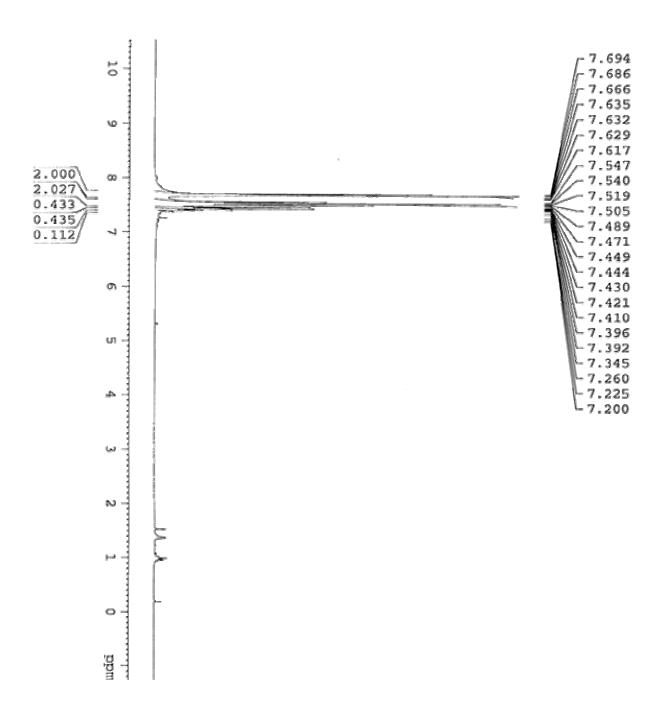


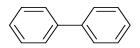
Biphenyl-2-carbaldehyde (in CDCl<sub>3</sub>)



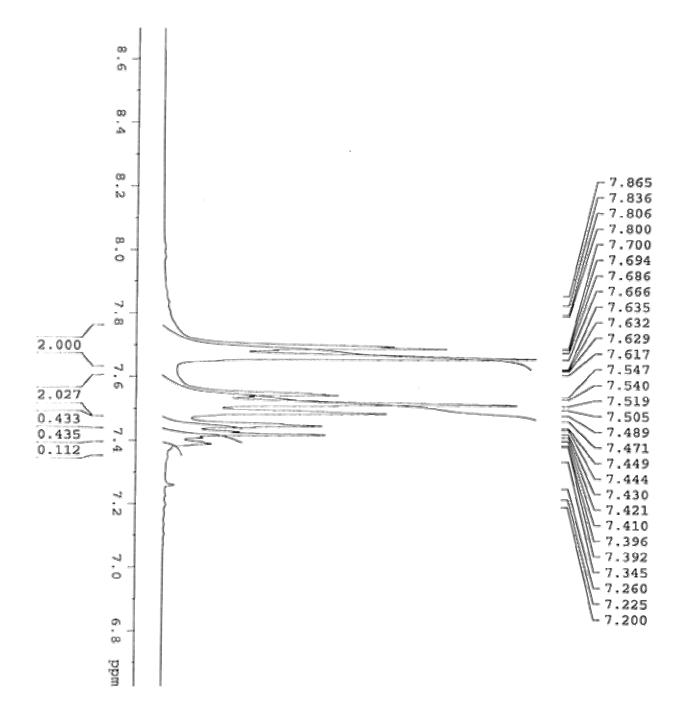


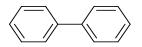
Biphenyl (in CDCl<sub>3</sub>)



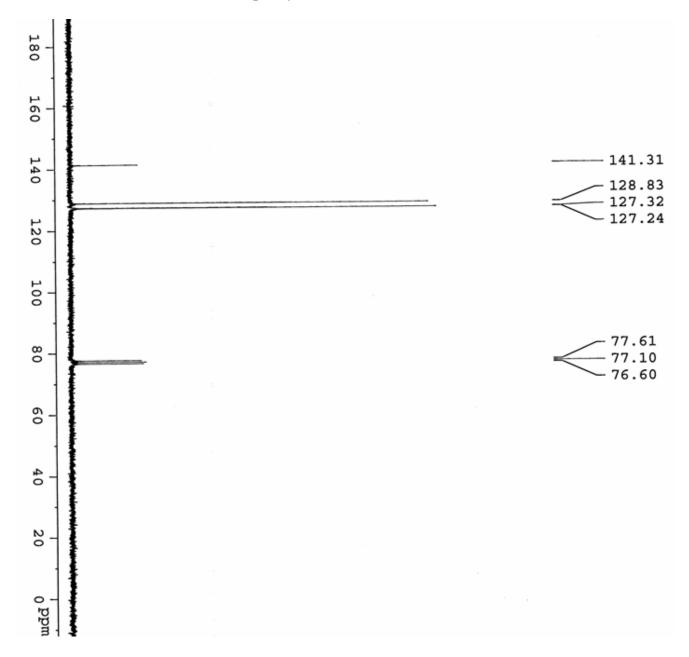


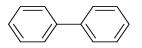
Biphenyl (in CDCl<sub>3</sub>)



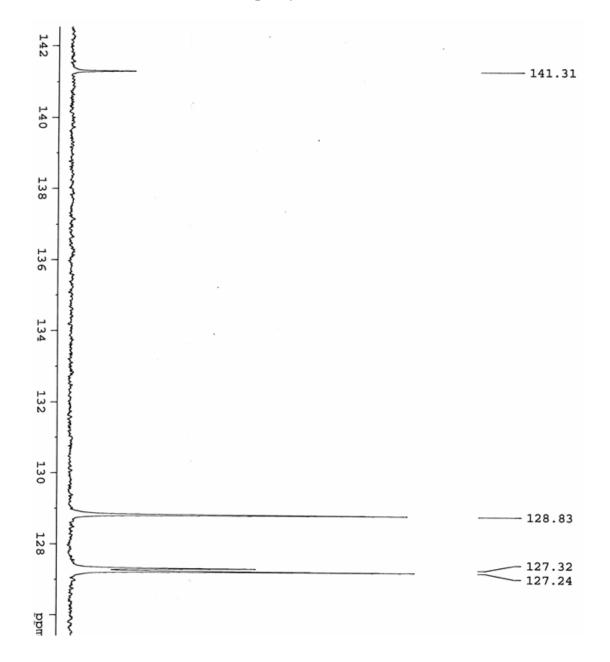


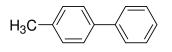
Biphenyl (in CDCl<sub>3</sub>)



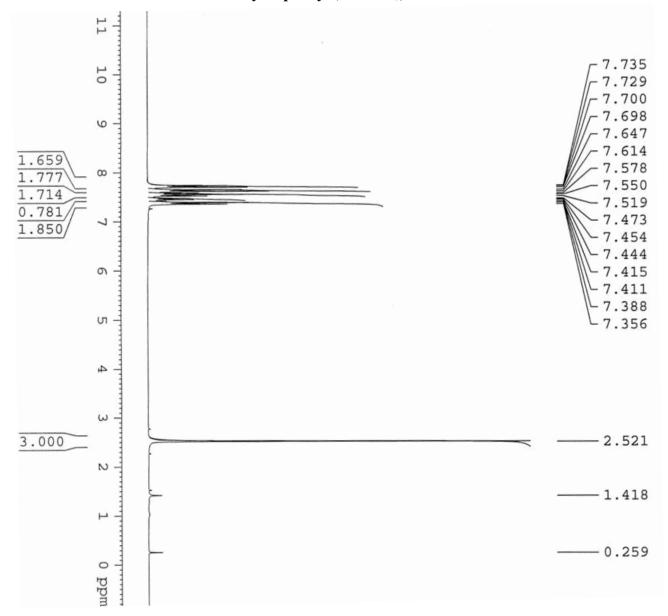


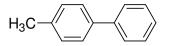
Biphenyl (in CDCl<sub>3</sub>)



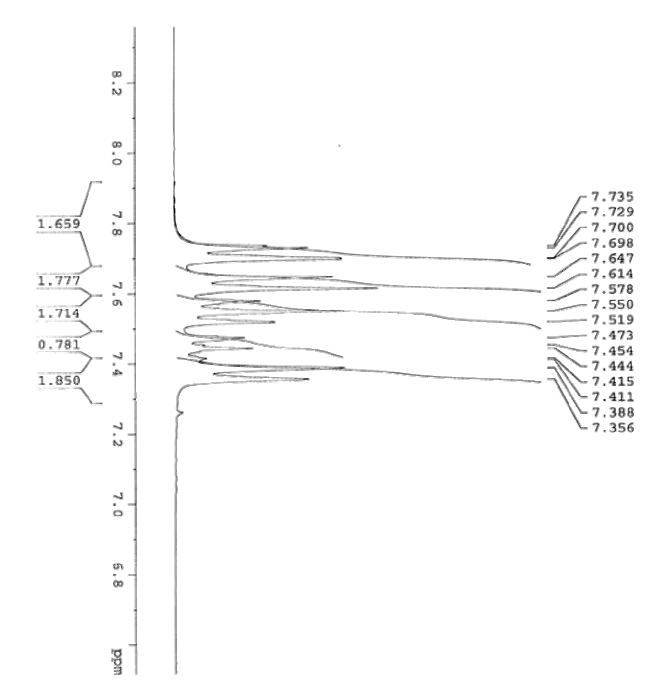


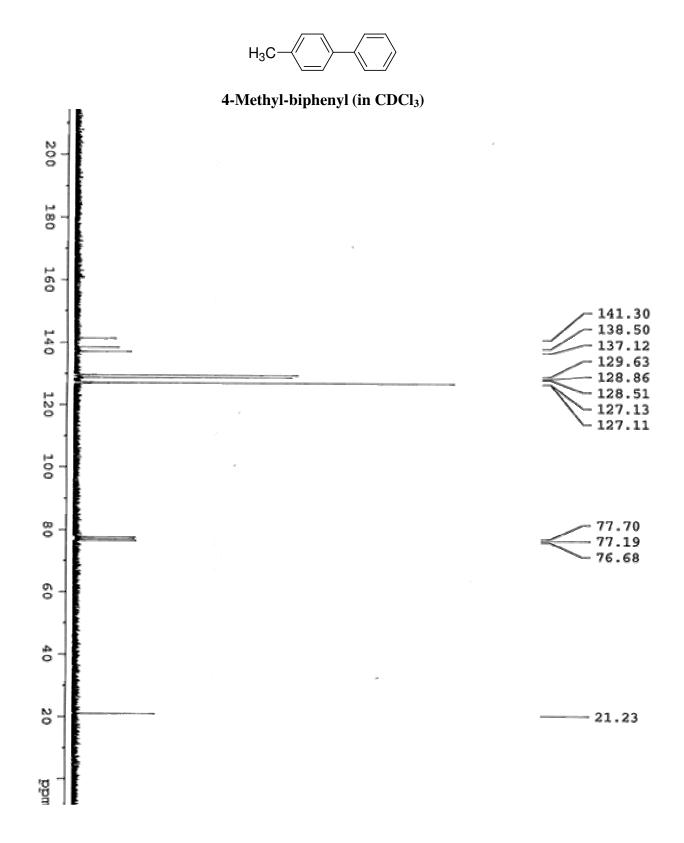
4-Methyl-biphenyl (in CDCl<sub>3</sub>)

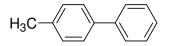




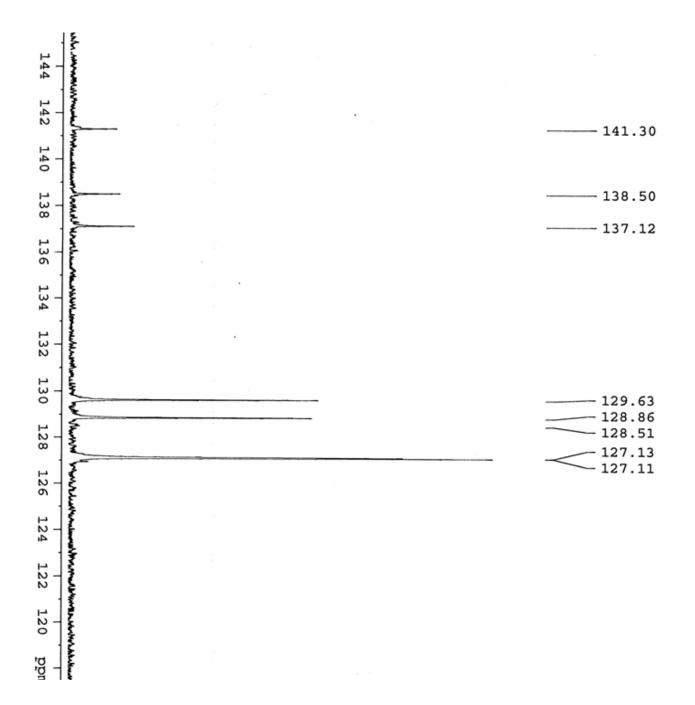
4-Methyl-biphenyl (in CDCl<sub>3</sub>)











## **References:**

- 1- Huynh, H. V.; Wong, L. R.; Ng, P. S. Organometallics 2008, 27, 2231.
- 2- Xu, L.; Chen, W.; Xiao, J. Organometallics 2000, 19, 1123.