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SUPPORTING INFORMATION

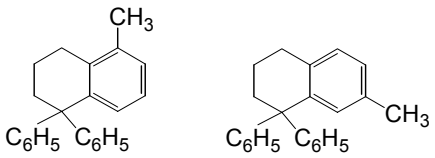
Title: Brønsted Acid Mediated Double Friedel–Crafts Reaction of Methylenecyclopropanes with Arenes
Author(s): Bao-Yu Wang, Ri-Shan Jiang, Jia Li, Min Shi*
Ref. No.: O200500261

Experimental Procedures:

General Methods. Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz respectively. Mass spectra were recorded by EI method, and HRMS was measured on Kratos Analytical Concept mass spectrometer (EI), and IonSpec 4.7 Tesla FFMS (MALDI). Organic solvents used were dried by standard methods when necessary. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Yinlong GF254 silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure.

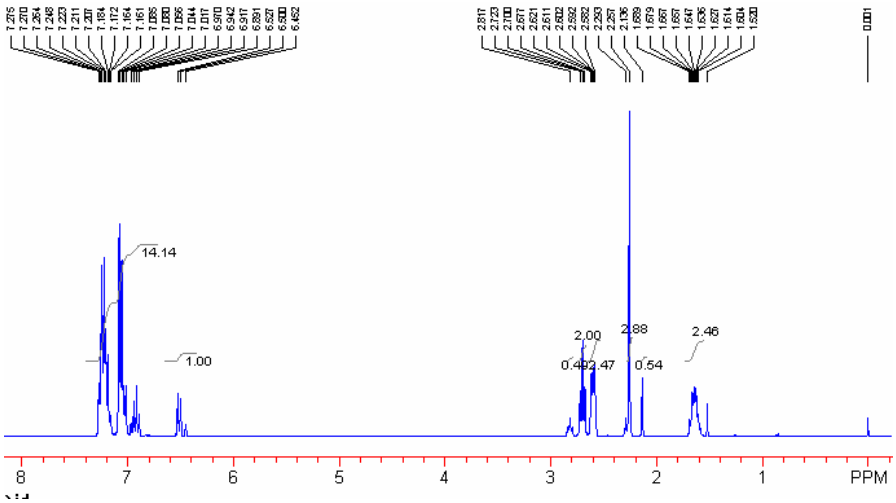
General Procedure for the Triflic acid catalyzed Friedel-Crafts Reactions of Methylenecyclopropanes with Arenes.

The mixture of MCP (0.4 mmol), CF_3SO_3H (0.4 mmol) and Arene (2.0 mL) were stirred for 1.5-8 hours at 30-85 ^{o}C. The solvent was removed under reduced pressure and the residue was purified by a silica gel column chromatography using petroleum as eluent to give the product.



5-Methyl-1,1-diphenyl-1,2,3,4,-tetrahydronaphthalene 2a-1 and

7-Methyl-1,1-diphenyl-1,2,3,4,-tetrahydronaphthalene 2a-2



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Sample directory: w-6-16_09Dec2004
File: NOESY

Pulse Sequence: NOESY

Solvent: CDCl3
Ambient temperature
Mercury-300BB "OMC300"

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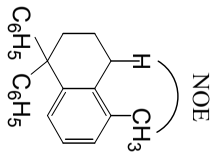
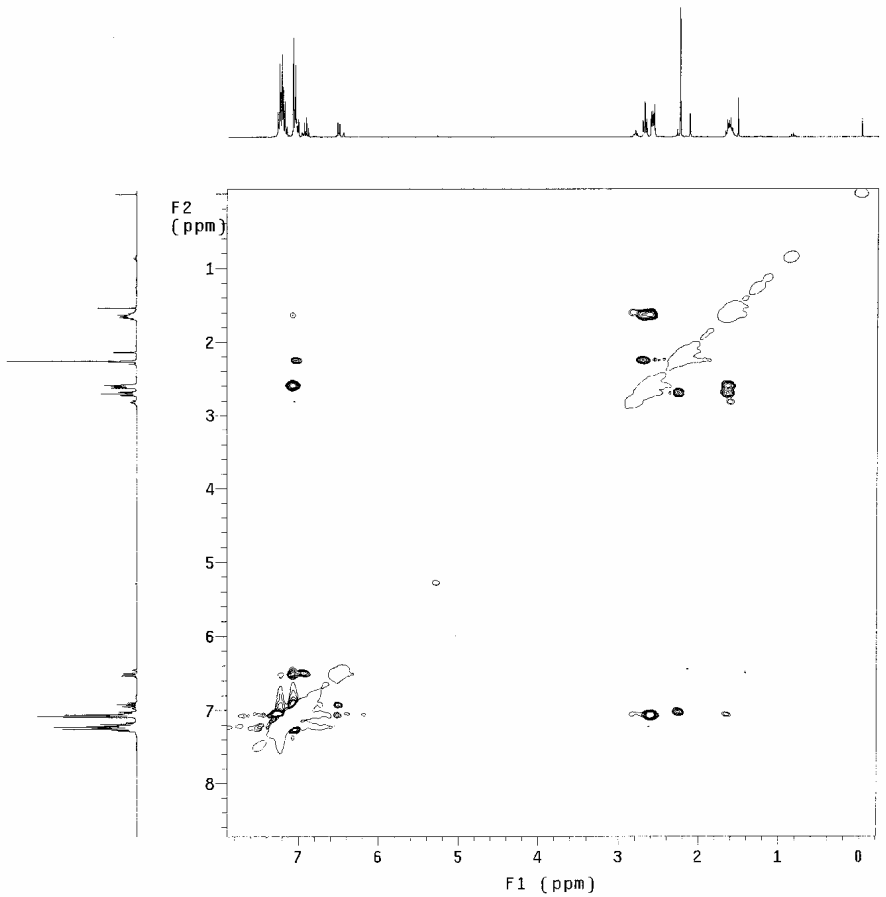
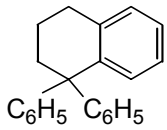
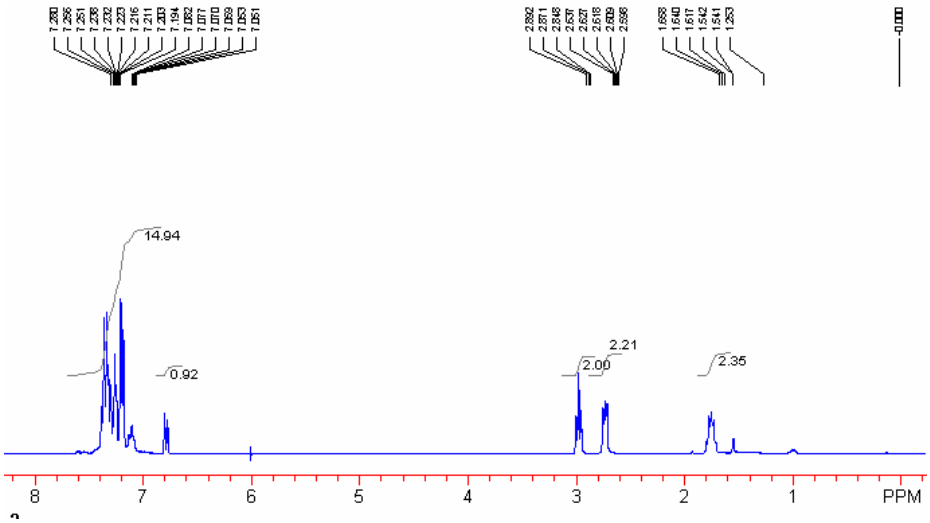
Mixing 0.800 sec
Acq. time 0.213 sec
Width 4807.7 Hz
2D Width 4807.7 Hz
32 repetitions
2 x 128 increments
OBSERVE H1, 300.0279816 MHz
DATA PROCESSING
Gauss apodization 0.034 sec
F1 DATA PROCESSING
Gauss apodization 0.025 sec
FT size 2048 x 2048
Total time 7 hr, 24 min, 27 sec

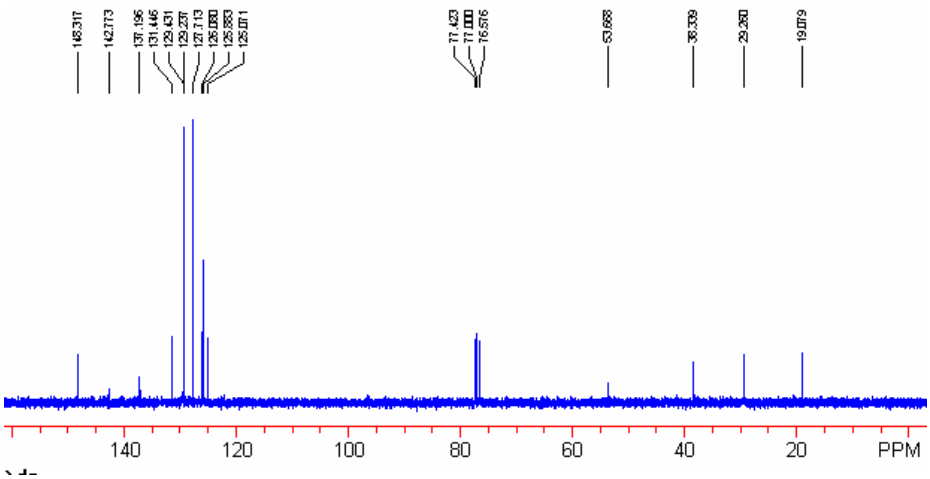


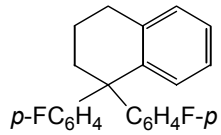




1,1-Diphenyl-1,2,3,4,-tetrahydronaphthalene 2b







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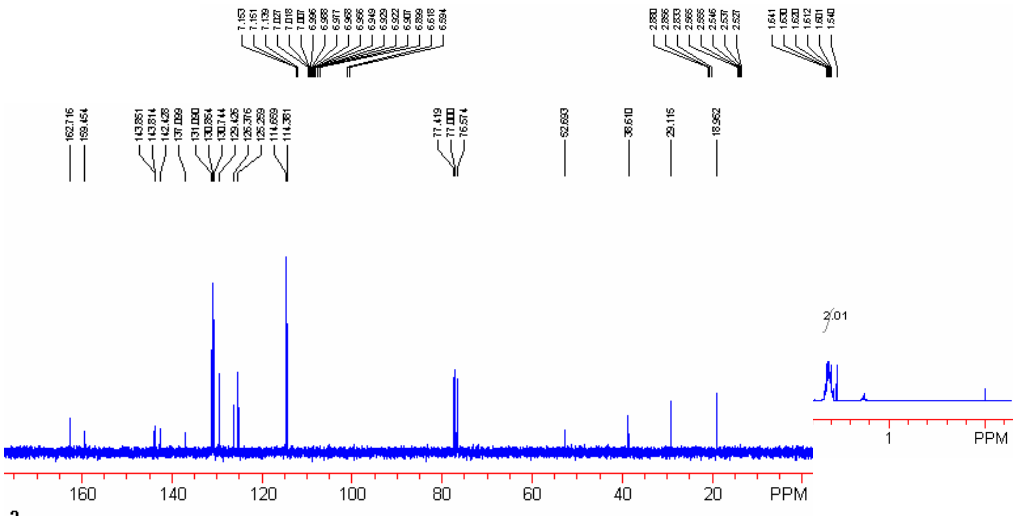
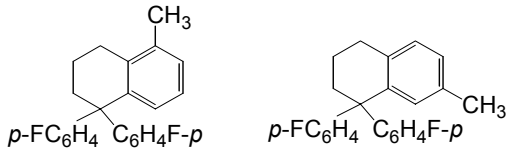
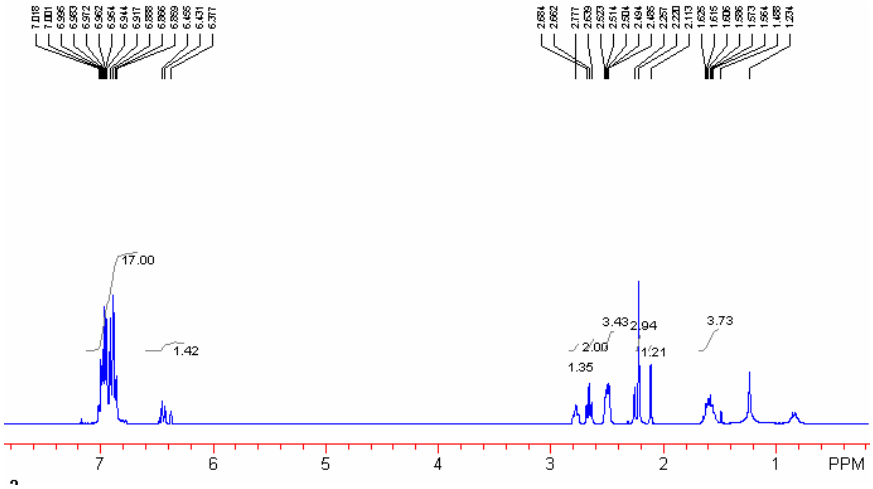
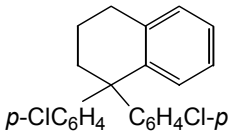




1,1-Bis(4-fluorophenyl)-5-methyl-1,2,3,4-tetrahydronaphthalene 2d-1 and

1,1-Bis(4-fluorophenyl)-7-methyl-1,2,3,4-tetrahydronaphthalene 2d-2





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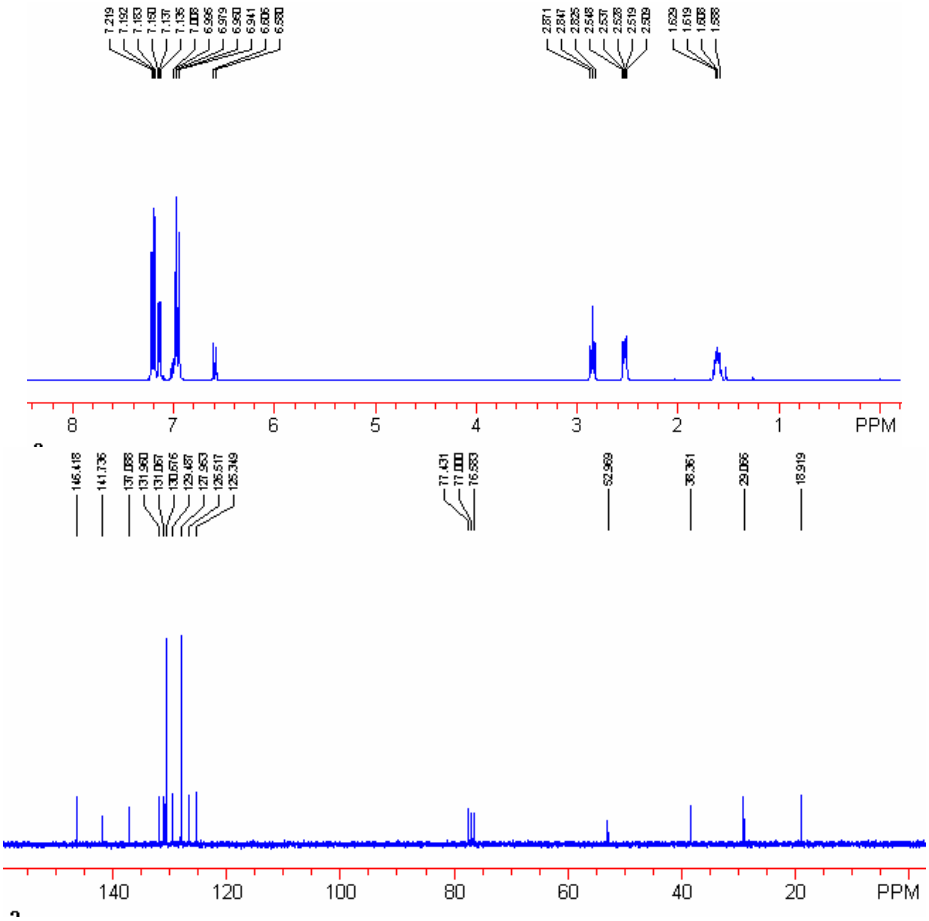
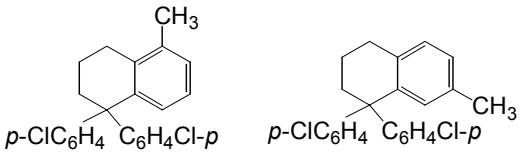
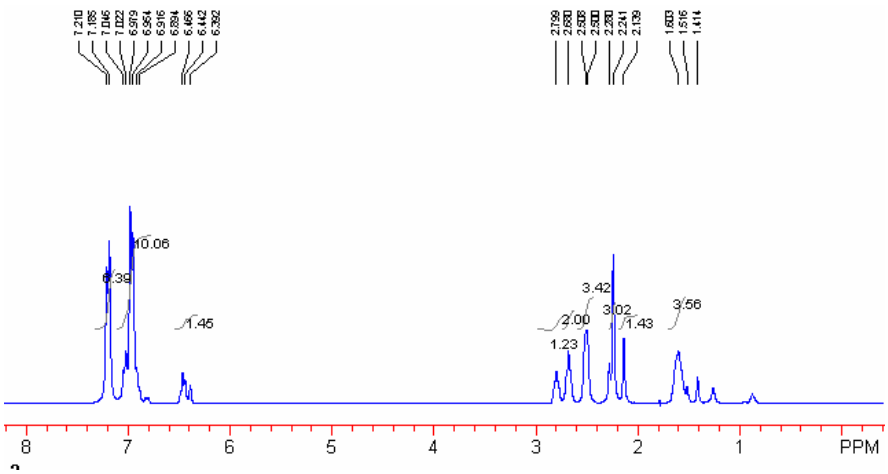
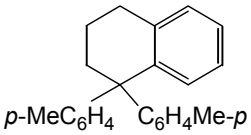




1,1-Bis(4-chlorophenyl)-5-methyl-1,2,3,4-tetrahydronaphthalene 2f-1 and

1,1-Bis(4-chlorophenyl)-7-methyl-1,2,3,4-tetrahydronaphthalene 2f-2





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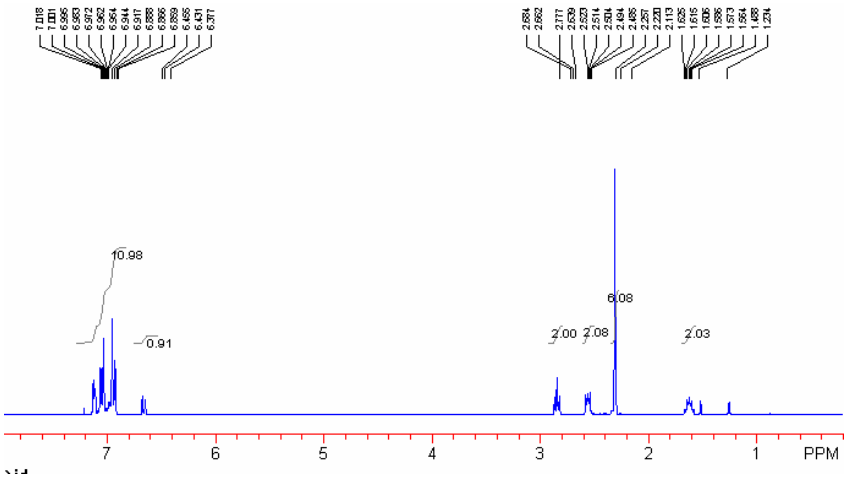

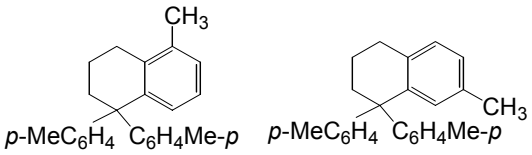

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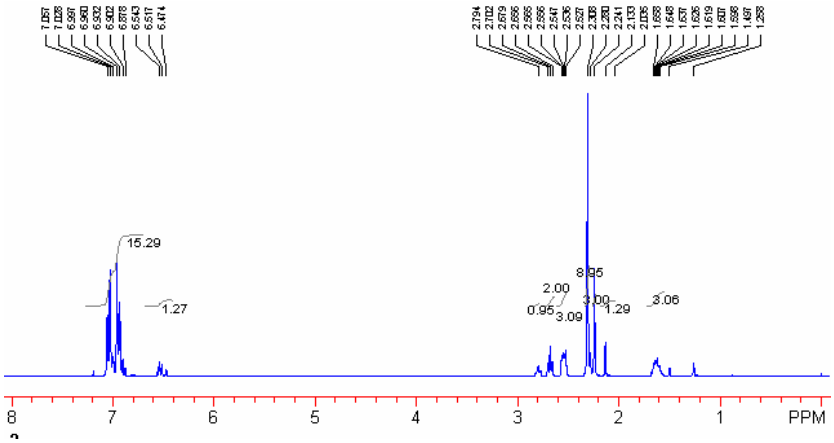
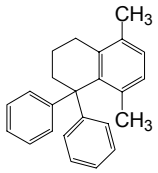
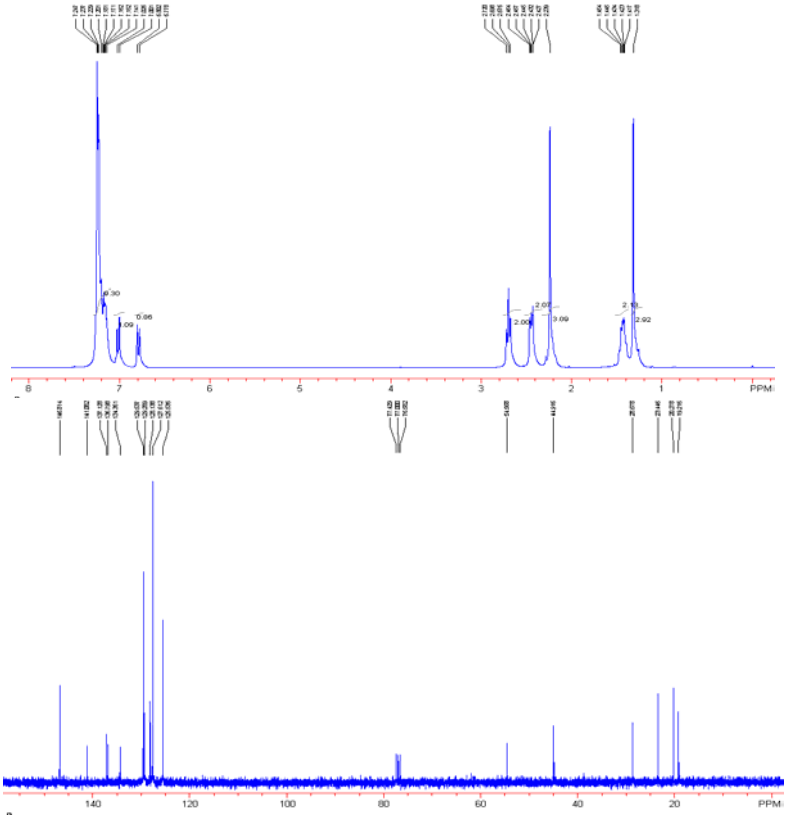
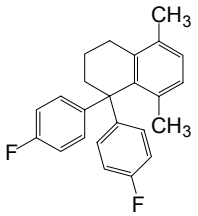
7-Methyl-1,1-di-*p*-tolyl-1,2,3,4-tetrahydronaphthalene 2h-2





5,8-Dimethyl-1,1-diphenyl-1,2,3,4-tetrahydronaphthalene 2i





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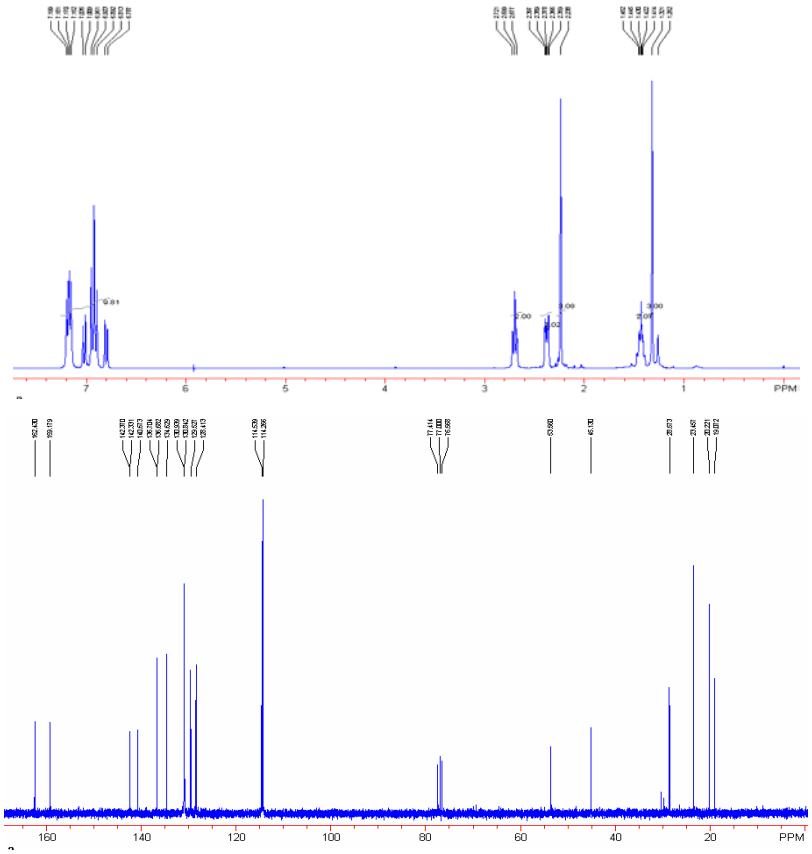

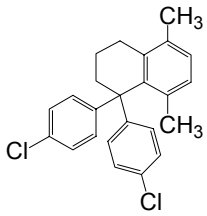

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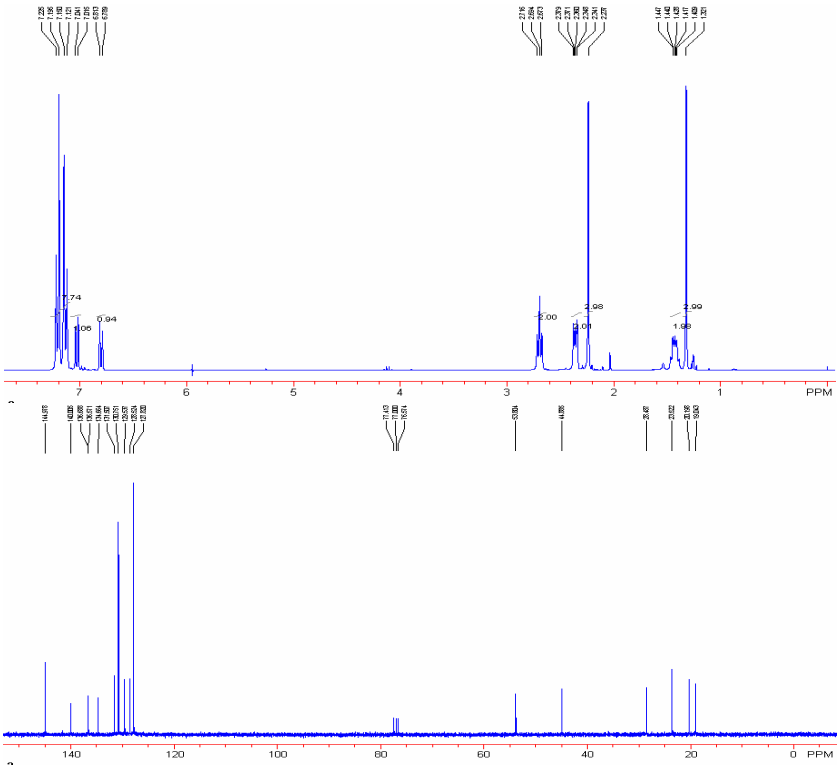
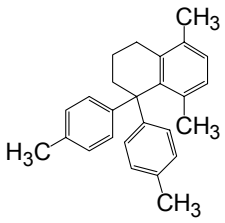
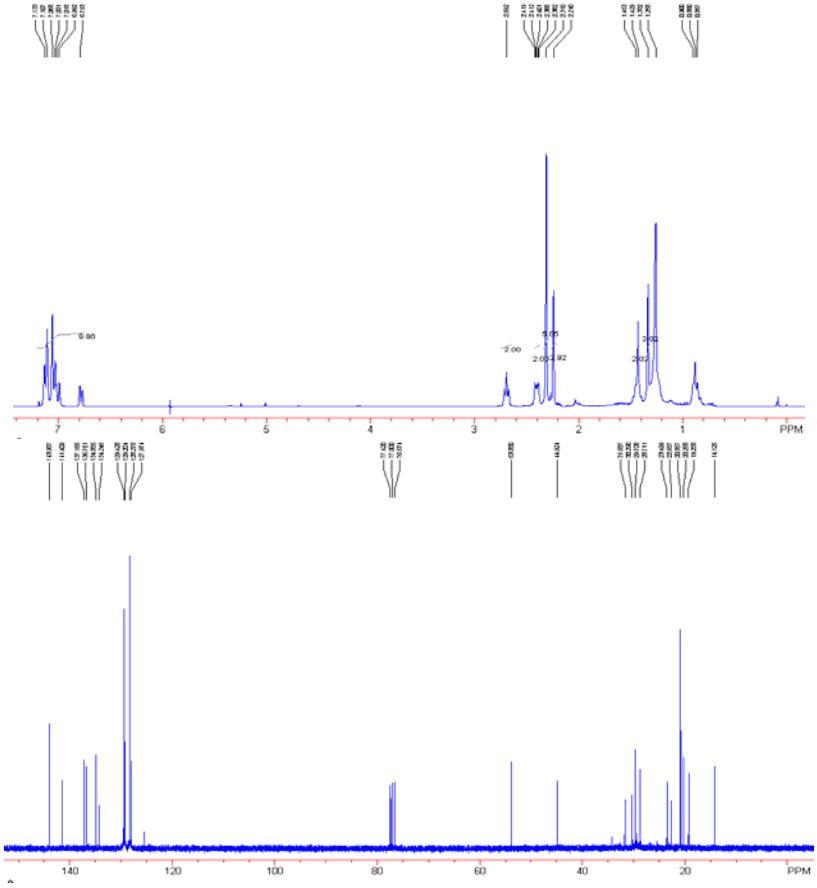
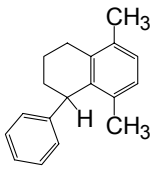


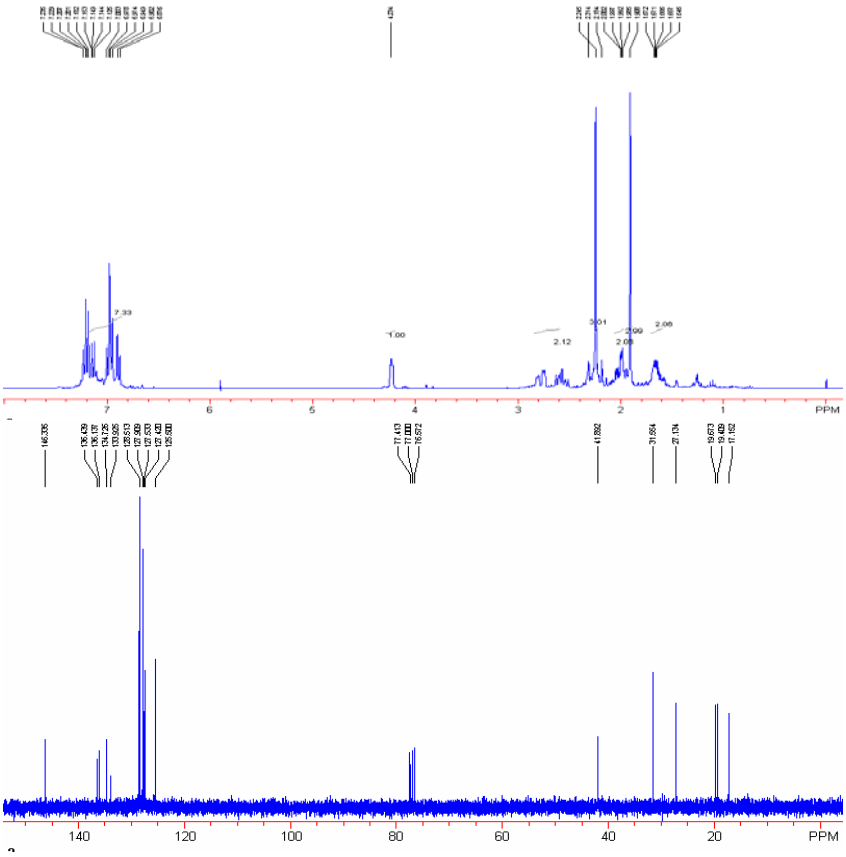


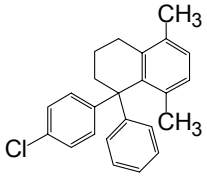
5,8-Dimethyl-1,1-di-*p*-tolyl-1,2,3,4-tetrahydronaphthalene 2l.





5,8-Dimethyl-1-phenyl-1,2,3,4-tetrahydronaphthalene 2m.





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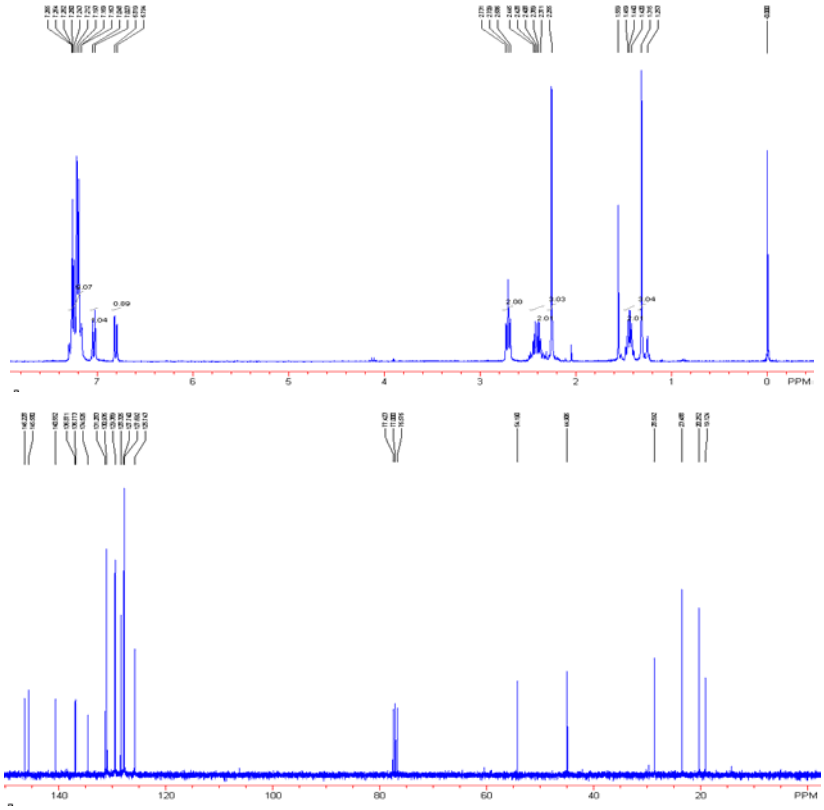

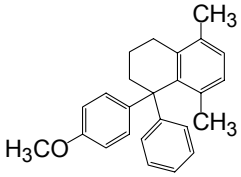

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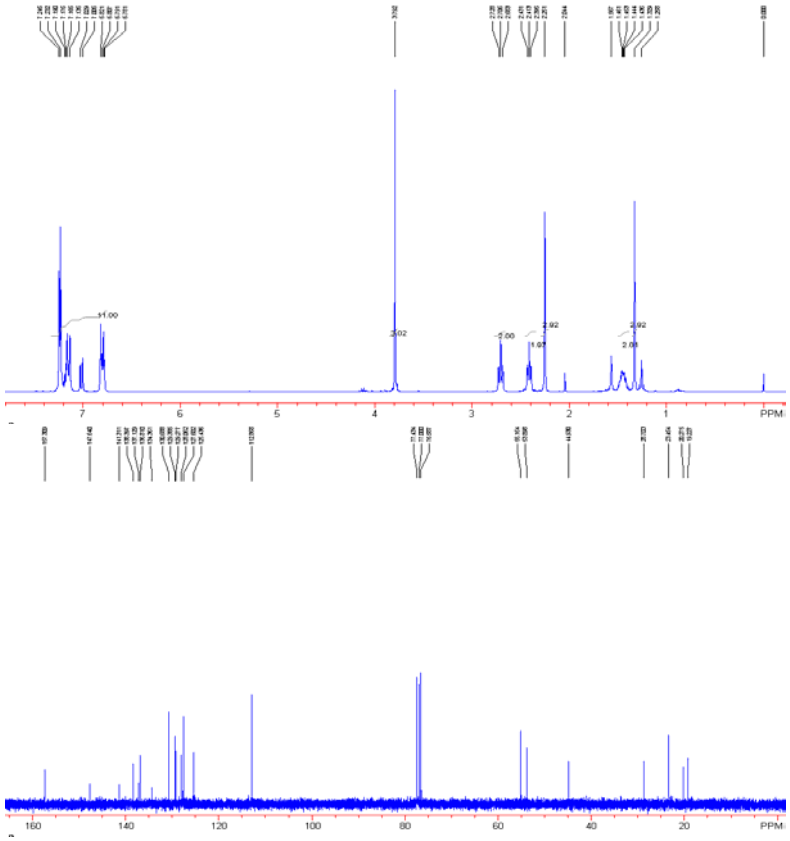

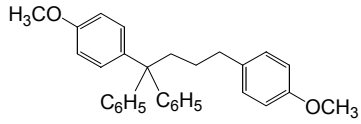
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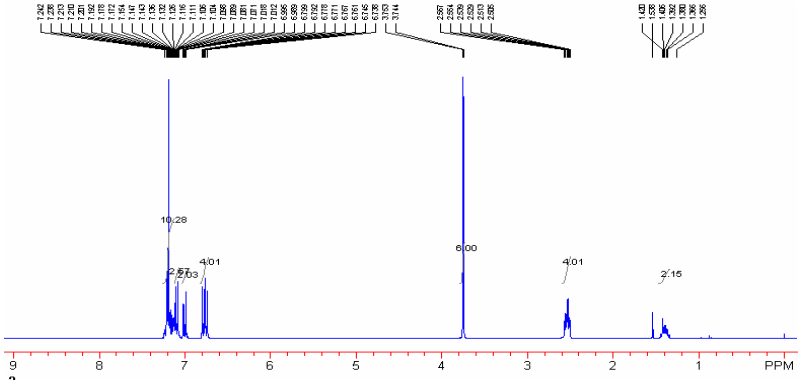
C6H5
OCH3

3a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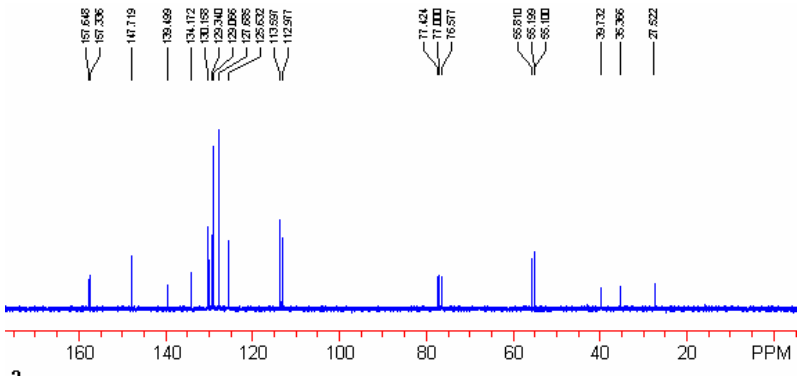
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77.000
76.577
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140
120
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80
60
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20
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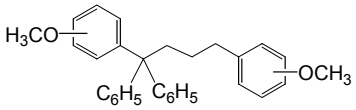
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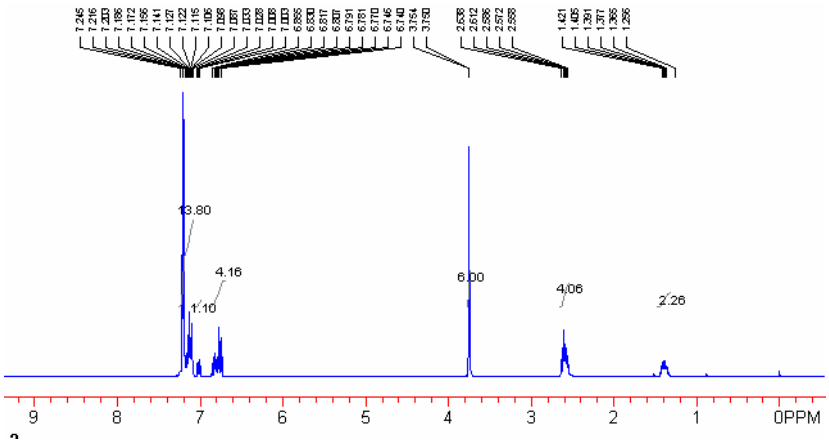
OCH3
C6H5
C6H5

3b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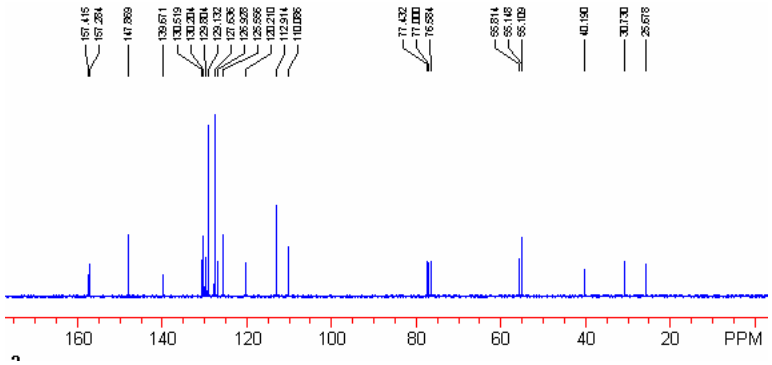
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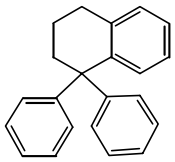
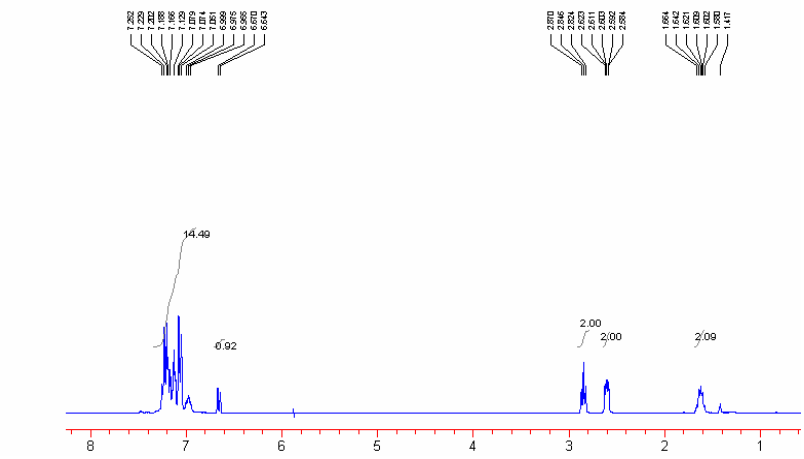


2b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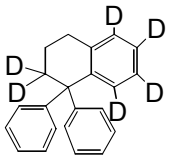
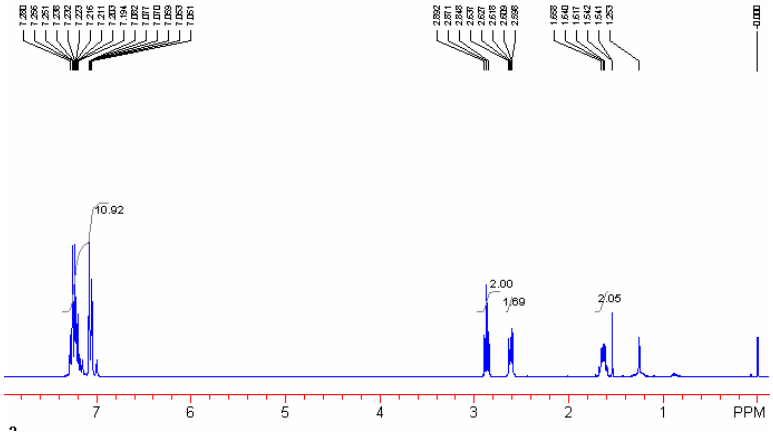
(15%) 
D
D
D
D
D
D

2b-*d*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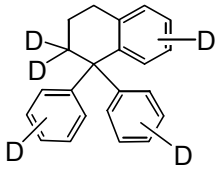
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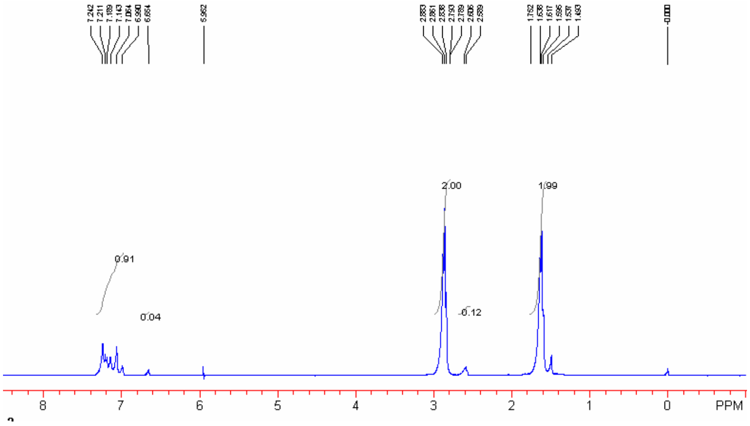
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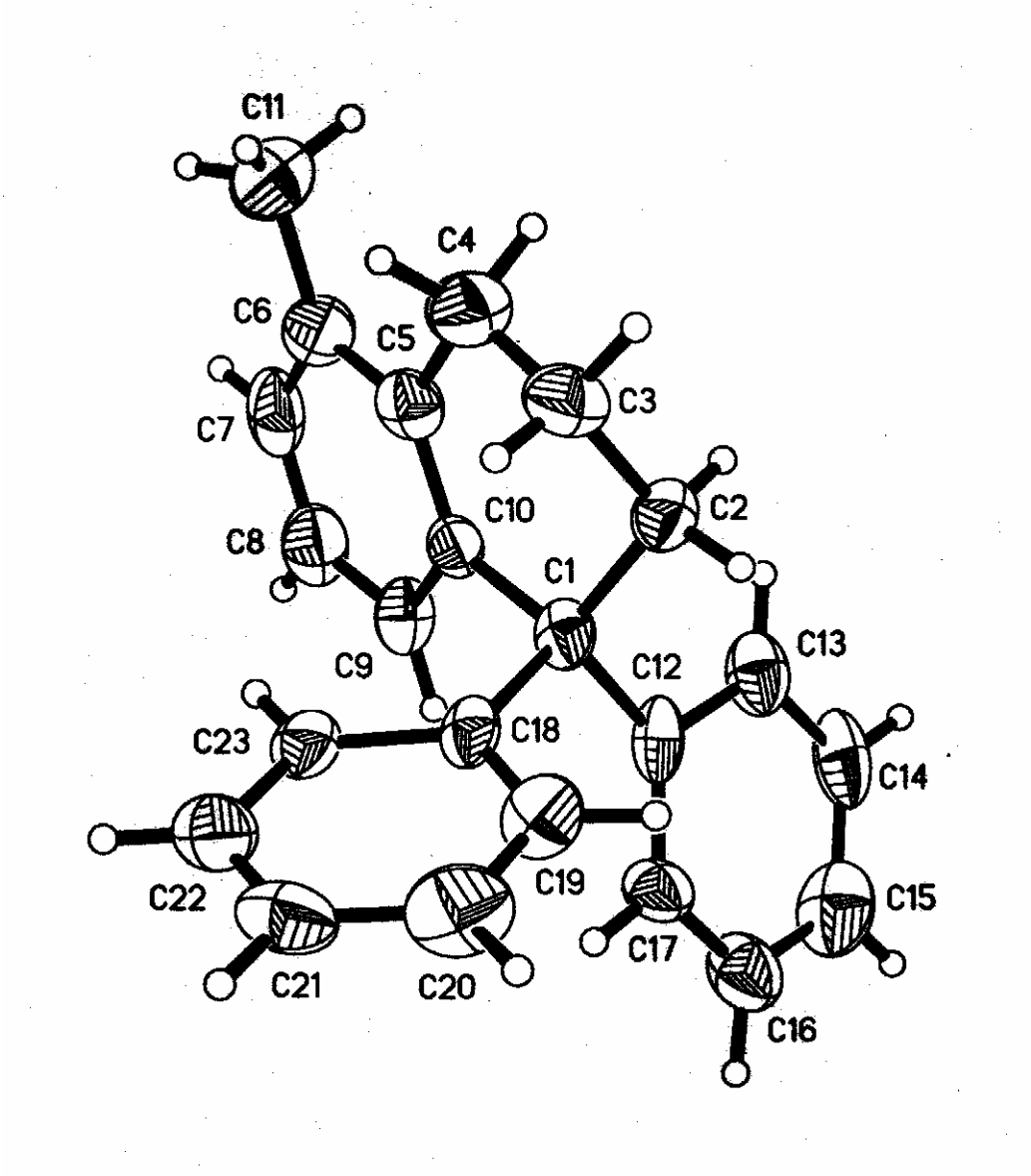

The crystal data of **2a-1** has been deposited in CCDC with number 249890. Empirical Formula: $C_{23}H_{22}$; Formula Weight: 298.41; Crystal size: 0.506 x 0.326 x 0.225; Crystal Color, Habit: colorless, prismatic; Crystal System: Monoclinic; Lattice Type: Primitive; Lattice Parameters: a= 26.41(2)Å, b= 7.350(6)Å, c= 19.375(16)Å, α= 90°, β= 114.894(14)°, γ= 90°, V= 3411(5)Å^3; Space group: Cc; Z= 8; D_{calc}= 1.162 g/cm^3; F_{000}= 1280; Diffractometer: Rigaku AFC7R.