Electronic supplementary information:

Engineering Supramolecular Organic Frameworks (SOFs) of *C*-alkylPyrogallol[4]arene with Bipyridine-based Spacers

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Materials and methods:

The XRD data was collected on a Bruker Apex II CCD diffractometer at a temperature of 100(2) K using CuKα radiation incotec Microfocus II (0.71073Å). The structure was solved and refined using SHELX with X-Seed as the interface. The general synthetic procedure of all frameworks is explained in more detail below, and the crystal structure details and CIF files are given in electronic supporting information.

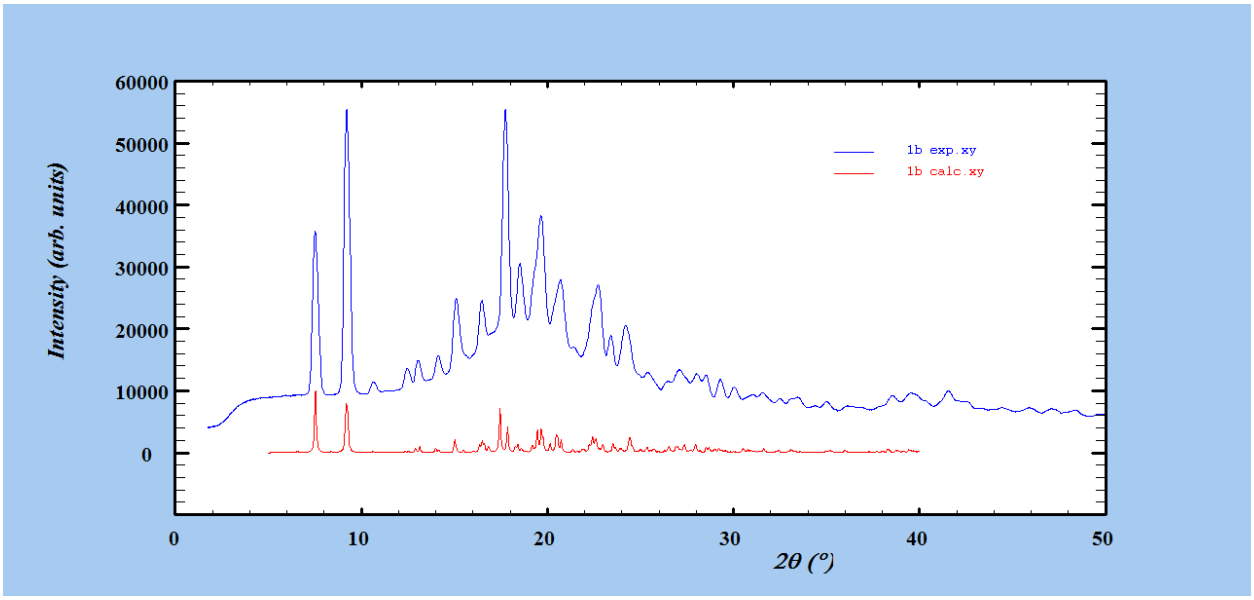
Thermogavimetric analysis is carried out on TA(TGA Q50) instrument with the temperature ranging from 15°C to 350°C of the 2mg-4mg sample. ^{1}H NMR analysis is carried out on Bruker DRX 300 instrument with *d6*-DMSO as a deuterated solvent.

General procedure of growing crystals: In a 20 ml glass vial, 2ml of 0.005M solution of PgC in acetonitrile or acetonitrile/toluene (9:1) mixture was mixed with 2ml of 0.01M solution (in acetonitrile) of spacer molecule. The clear mixture was then sonicated for 5 min and allowed to stand for slow solvent evaporation. Crystals suitable for scXRD were obtained over 8-10 days. Similar procedures were followed to grow the crystals for all the frameworks described in the article.

Crystallographic data of frameworks:

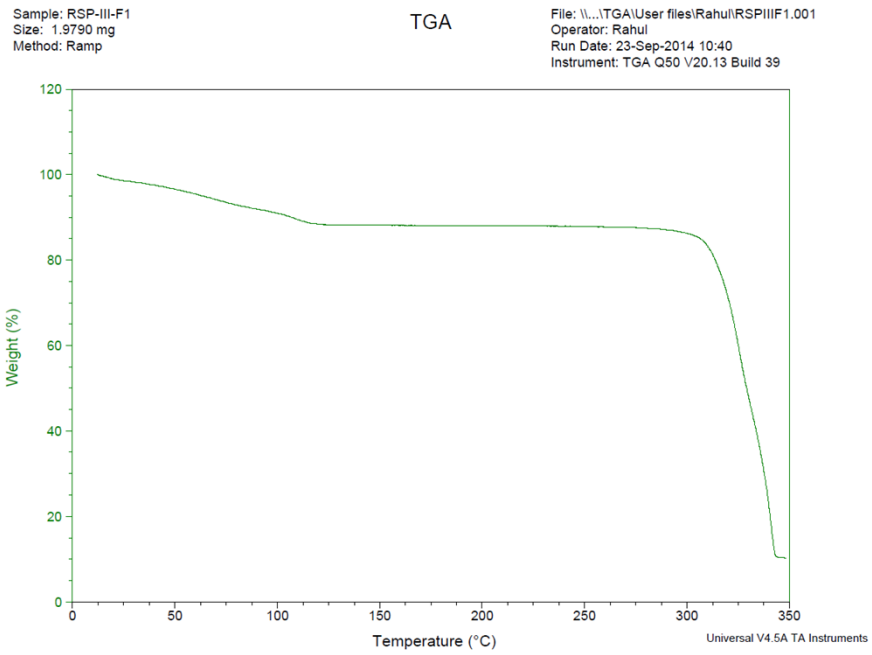
	1a	1b	2a	2b
Molecular formula	$C_{124}H_{134}N_{10}O_{24}$	$C_{146}H_{150}N_{10}O_{24}$	$C_{79}H_{64}N_{10}O_{12}$	$C_{168}H_{128}N_{20}O_{24}$
Formula weight	2148.48	2428.85	1345.44	2810.99
Crystal system	Monoclicic	Orthorhombic	Tetragonal	Monoclinic
Space group	P21/c	Pna21	P4/ncc	C2/c
Temp.(K)	100	100	100	100
a(Å)	21.1314	23.4514	21.6686	20.8301
b(Å)	15.228	16.4326	21.6686	12.6507
c(Å)	18.2707	16.8992	15.3857	29.0453
α(°)	90	90	90	90
β(°)	110.133	90	90	107.33
γ(°)	90	90	90	90
V(Å^3)	5517.04	6512.40	7424.02	7306.35
Z	2	2	4	2

PXRD: Overlay of experimental and calculated PXRD for sample **1b**

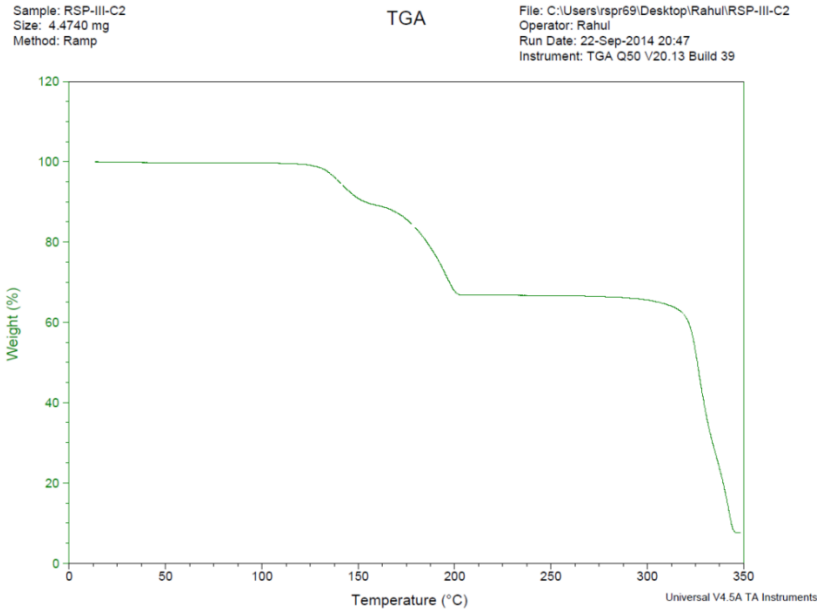


Thermogravimetric Analysis (TGA) Graphs:

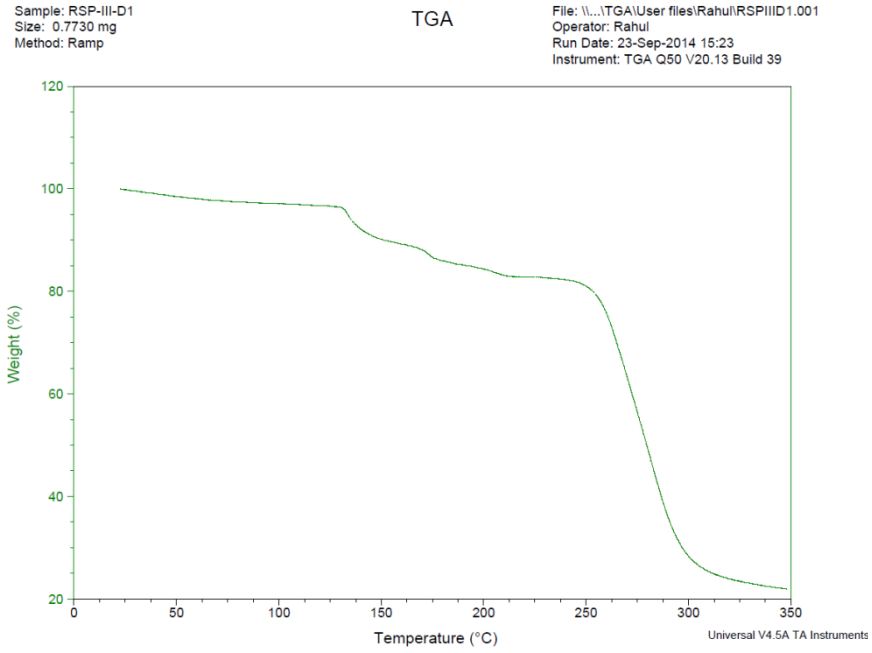
1. **1**



2. **1a**



3.**1b**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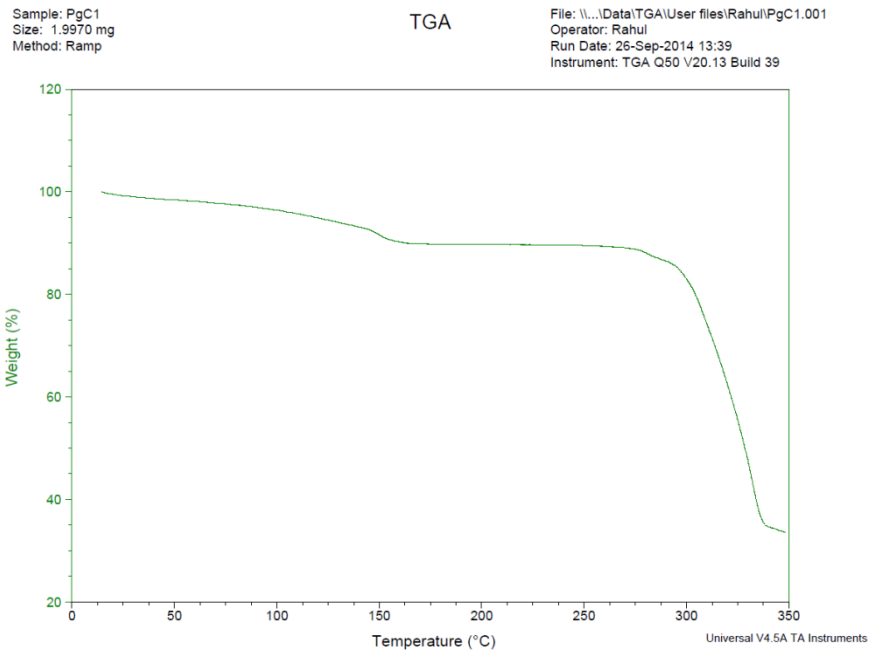
Size: 0.7730 mg
Method: Ramp
TGA
File: \\...\TGA\User files\Rahul\RSPIIID1.001
Operator: Rahul
Run Date: 23-Sep-2014 15:23
Instrument: TGA Q50 V20.13 Build 39
Weight (%)
Temperature (°C)
Universal V4.5A TA Instruments

4. **2**


Sample: PgC1
Size: 1.9970 mg
Method: Ramp
TGA
File: \\...\Data\TGA\User files\Rahul\PgC1.001
Operator: Rahul
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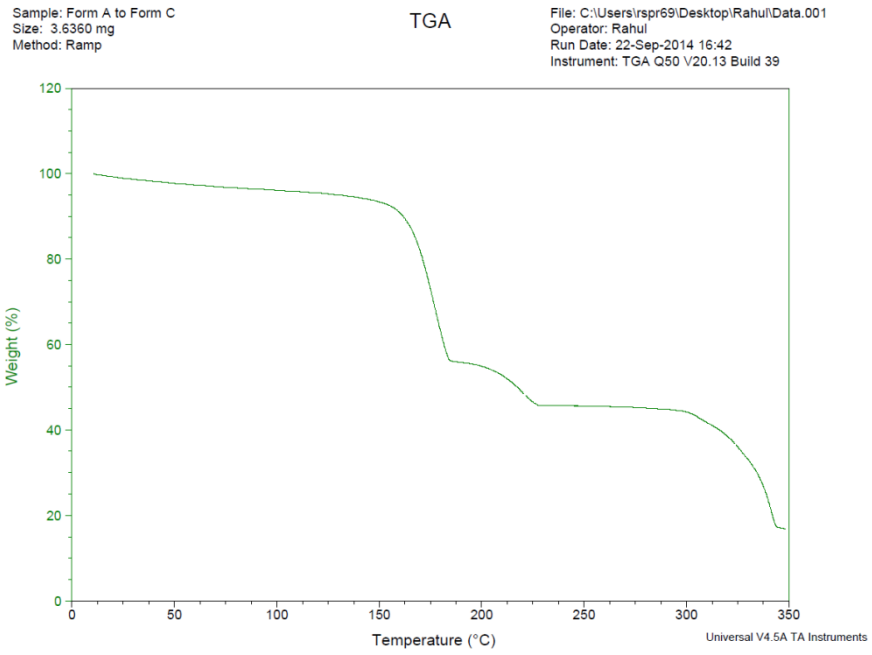
Instrument: TGA Q50 V20.13 Build 39
Weight (%)
Temperature (°C)
Universal V4.5A TA Instruments

5. **2a**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Size: 3.6360 mg
Method: Ramp
TGA
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Operator: Rahul
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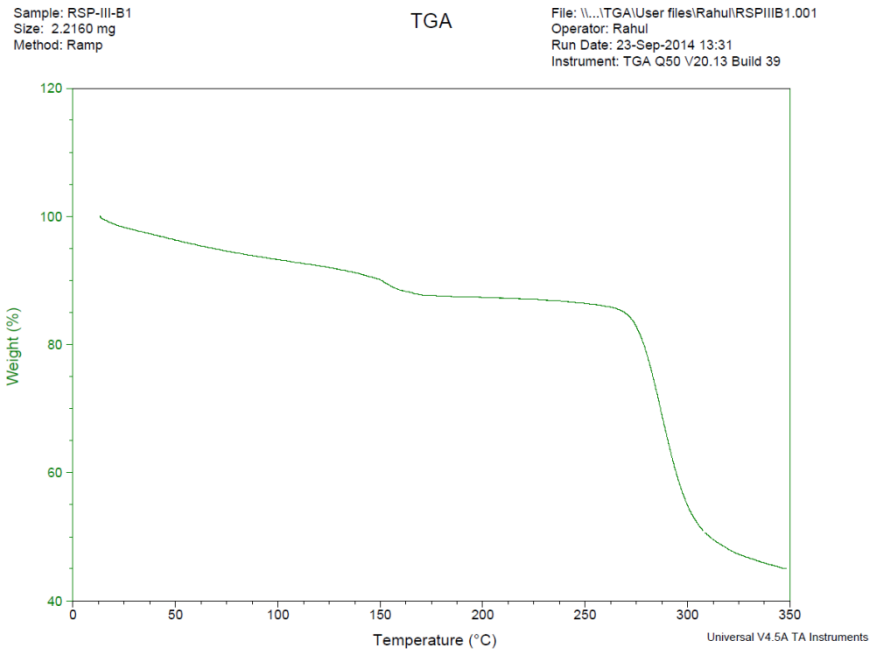
Instrument: TGA Q50 V20.13 Build 39
Weight (%)
Temperature (°C)
Universal V4.5A TA Instruments

6. **2b**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Size: 2.2160 mg
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TGA
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Operator: Rahul
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Instrument: TGA Q50 V20.13 Build 39
Weight (%)
Temperature (°C)
Universal V4.5A TA Instruments

1H NMR spectra:

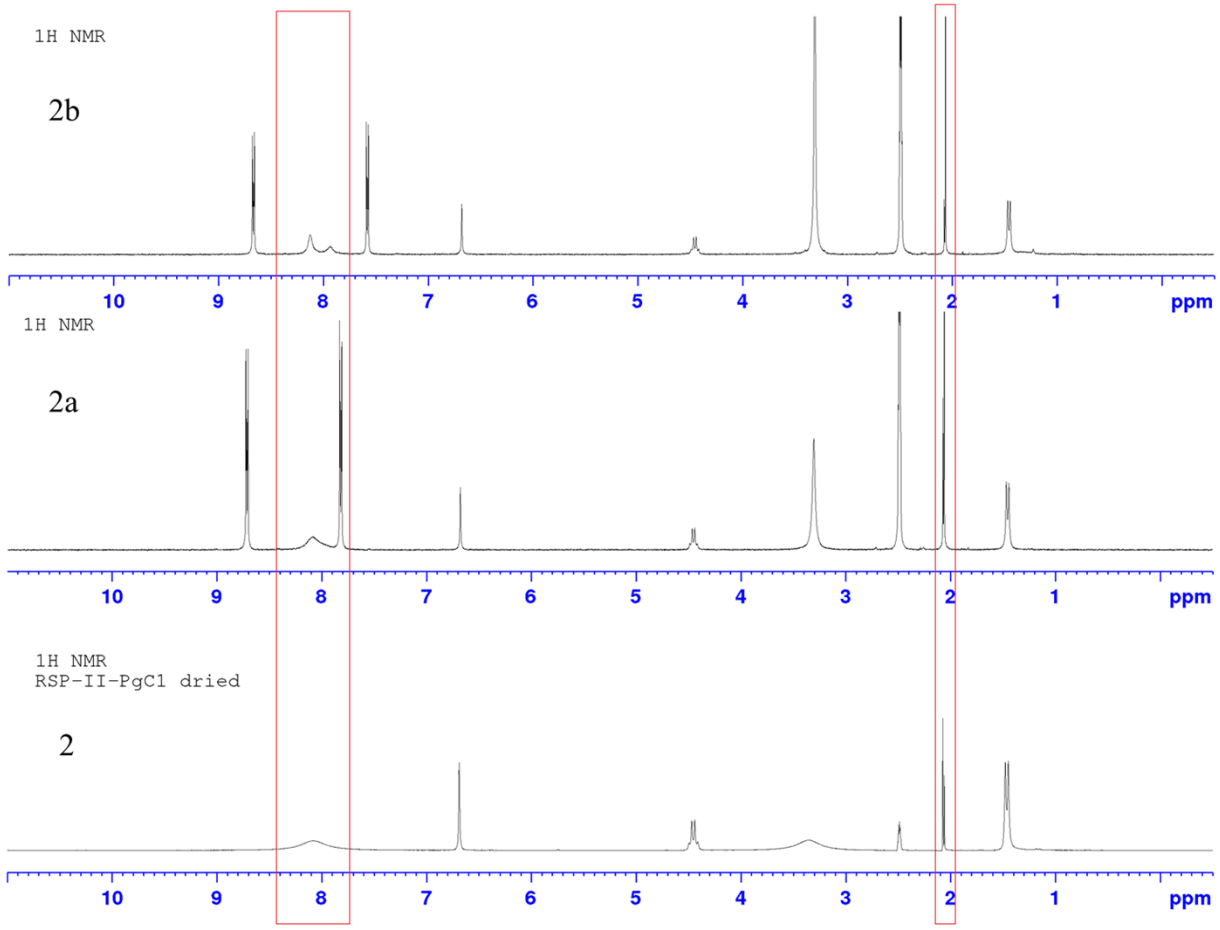
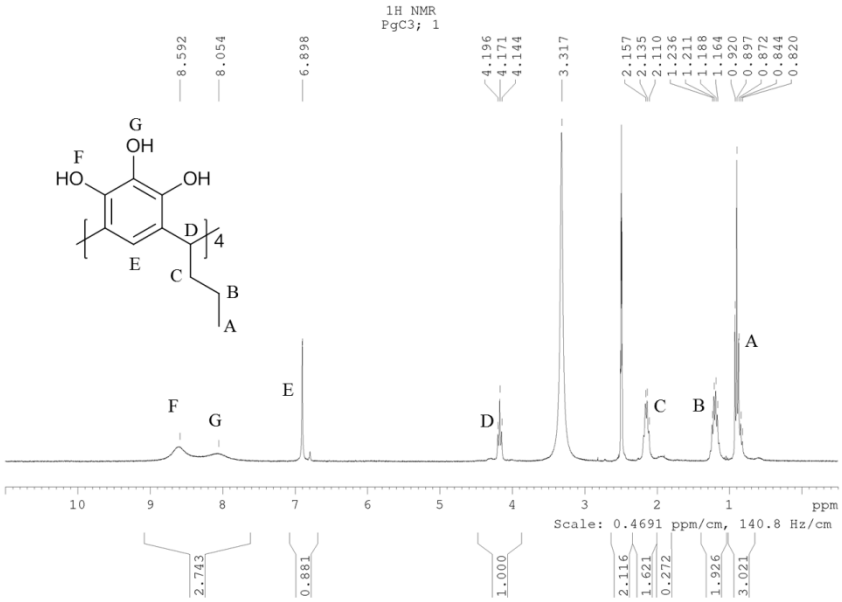


Table 1:Validation of weight loss in TGAwith 1H NMR data.

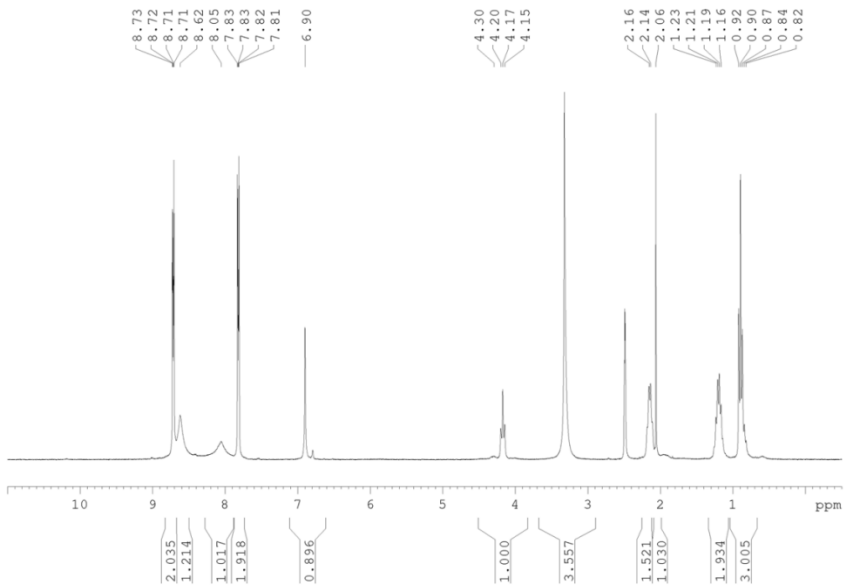
	1a	1b	2a	2b
Calculated solvent molecules/macrocycle	1 MeCN	1.5 MeCN, 0.7 Toluene	3.6 MeCN	2.3 MeCN, 2 water
% mass of solvent	4	9.6	11	12
%weight loss	5	10	10	10
Temperature	120 °C	150 °C	160 °C	150 °C

1H NMR spectra with integration:

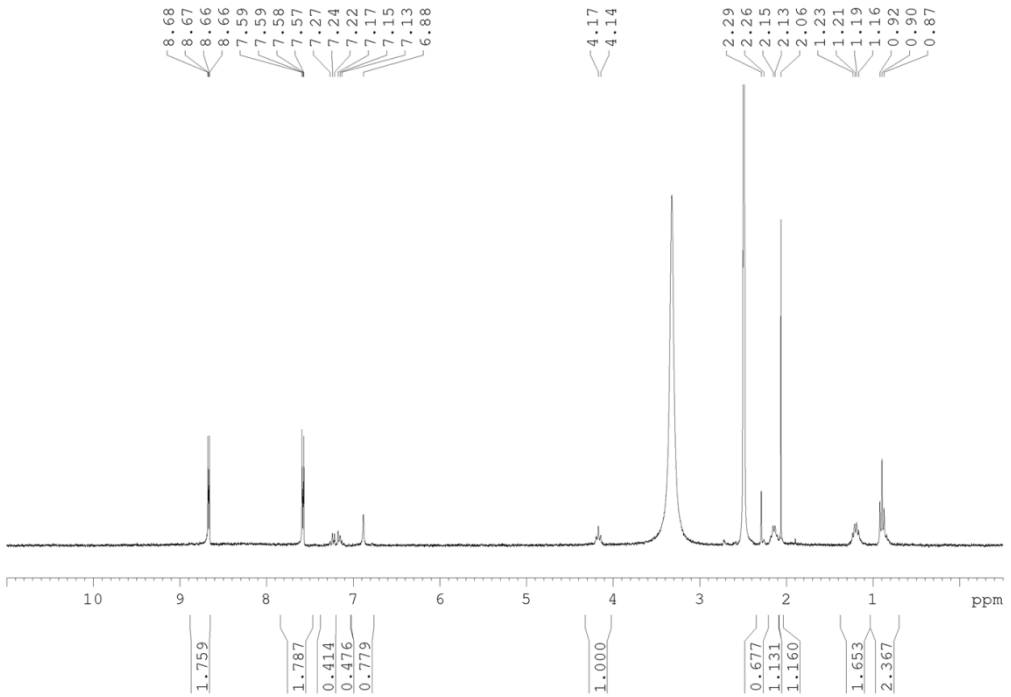
1.



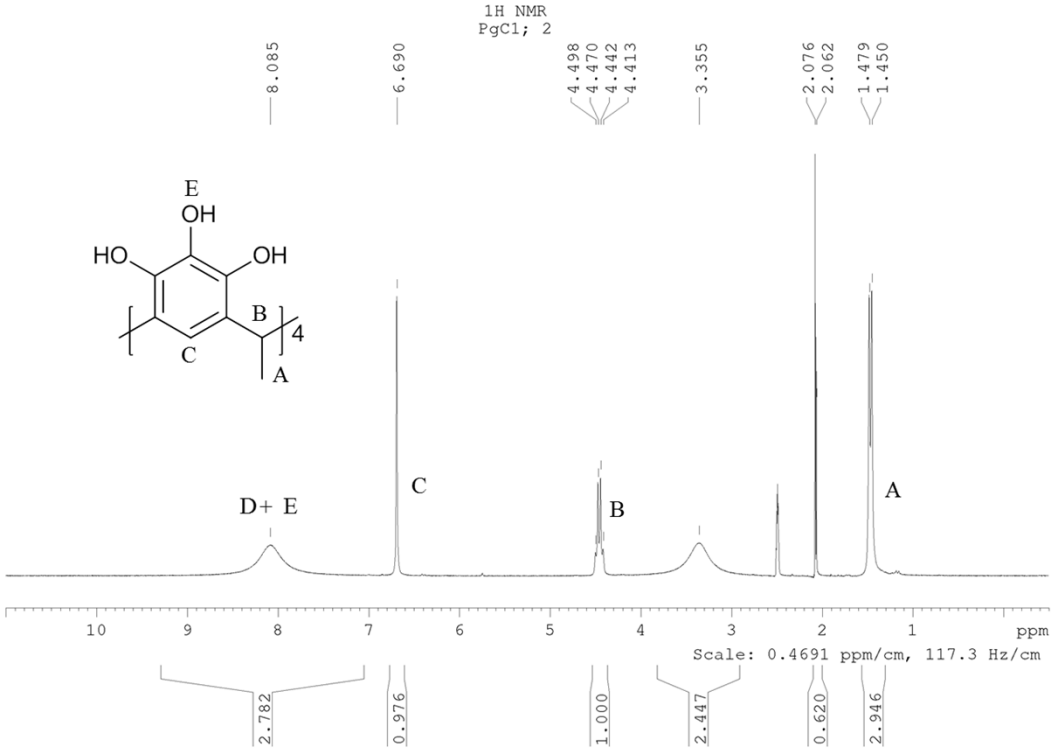
1a.



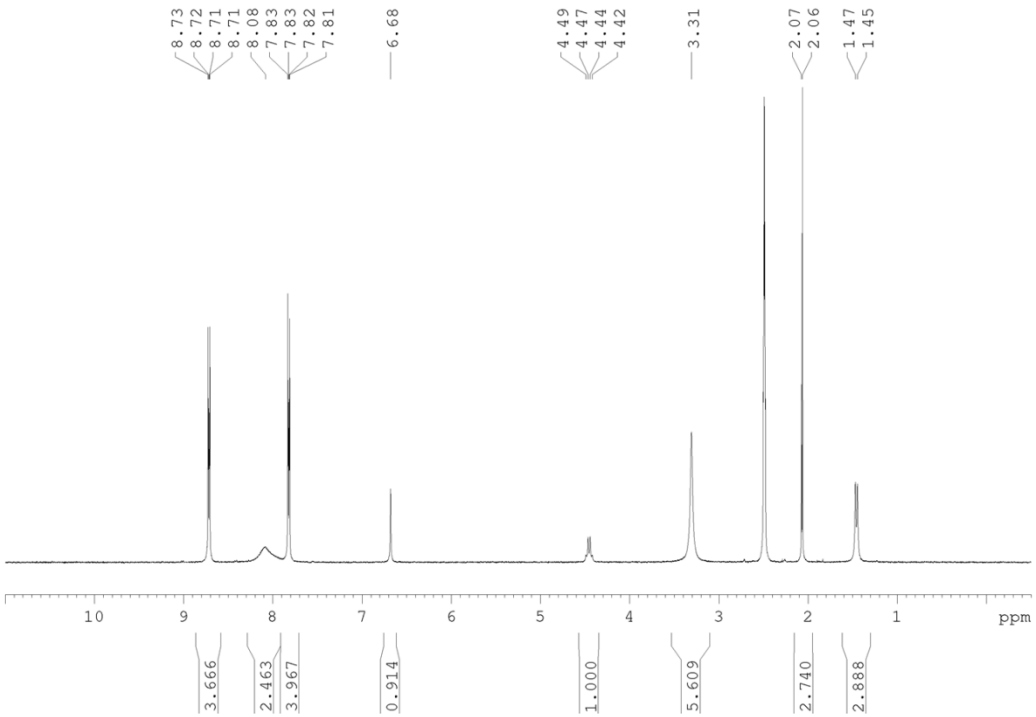
1b.


8.68
8.67
8.66
8.66
7.59
7.59
7.58
7.57
7.27
7.24
7.22
7.17
7.15
7.13
6.88
4.17
4.14
2.29
2.26
2.15
2.13
2.06
1.23
1.21
1.19
1.16
0.92
0.90
0.87
10
9
8
7
6
5
4
3
2
1
ppm
1.759
1.787
0.414
0.476
0.779
1.000
0.677
1.131
1.160
1.653
2.367

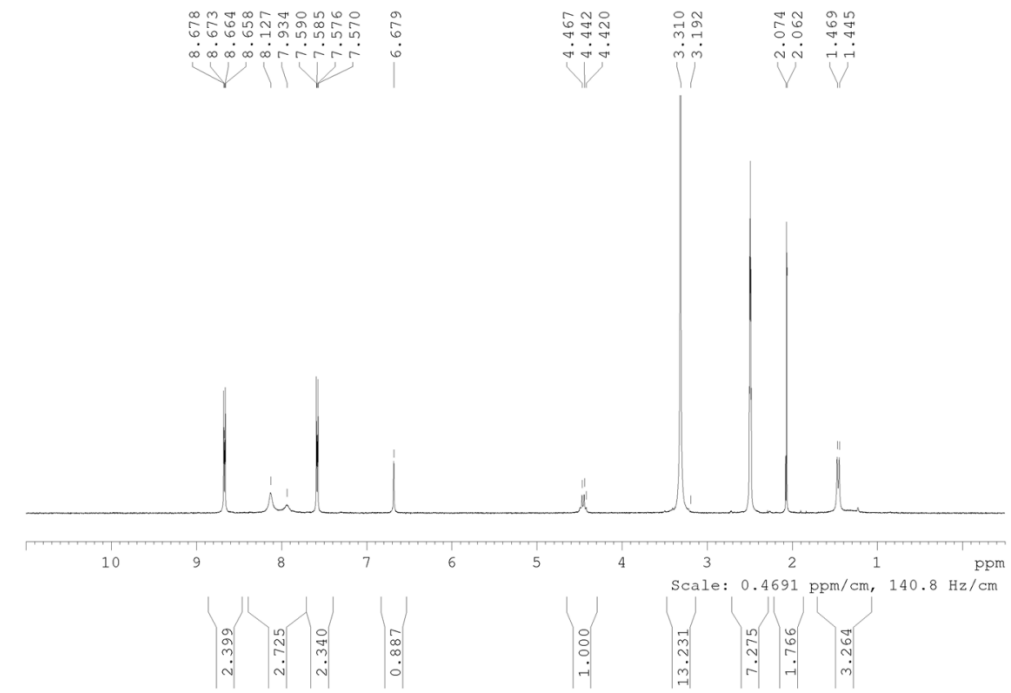
2.


1H NMR
PgC1; 2
8.085
6.690
4.498
4.470
4.442
4.413
3.355
2.076
2.062
1.479
1.450
E
OH
HO
OH
B
C
4
A
D+ E
C
B
A
10
9
8
7
6
5
4
3
2
1
ppm
Scale: 0.4691 ppm/cm, 117.3 Hz/cm
2.782
0.976
1.000
2.447
0.620
2.946

2a.



2b.



1: *C*-methylpyrogallol[4]arene, PgC1

2:*C*-propylpyrogallol[4]arene, PgC3

1a: [(PgC3).(bpy).(MeCN)]

1b: [(PgC3).(bpa).(MeCN.Toluene)]

2a: [(PgC1).(bpy).(MeCN)]

2b: [(PgC1).(bpa).(MeCN)]