Undecenyl resorc[4]arene in the *chair* conformation as preorganized synthon for olefin metathesis

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ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

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Table 1S. ^{1}H NMR and ^{13}C NMR signals* of undecenyl resorc[4]arene **1a** (*chair*)

Carbon	^{13}C	^{1}H
C=O	172.4	-
C_{Ar}–O	156.6	-
	155.8	
=CH	139.2	5.82 ddt (17.2, 10.2, 6)
CH_i (26,28)	126.6	6.19 s
CH_i (25,27)	125.7	6.82 s
C_{Ar}–C	125.3	-
	122.6	
=CH_2	114.3	4.99 br d (17.2)
		4.92 br d (10.2)
CH_e (5,17)	97.1	6.47 s
CH_e (11,23)	95.3	6.39 s
OCH_2	64.3	3.98 br t
		3.92 t
OMe	56.0	3.88 s
	56.0	3.64 s
CH_2-(CO)	39.6	2.73 dd (14.5, 10.5)
		2.65 dd (14.5, 6.5)
CH_2-(CH=)	34.0	2.05 q (6)
CH	33.0	5.04 dd (10.5, 6.5)
CH_2-(CH_2-CH=)	29.1	1.46 m
CH_2-(CH_2O)	28.7	1.38 m
$CH_2 \times 5$	29.6	1.24 br m
	29.6	
	29.5	
	29.3	
	26.0	

* 600 MHz (^{1}H) and 100 MHz (^{13}C), CDCl$_3$, T = 300 K; coupling constants J (Hz) are given in parentheses.

Table 2S. ^{1}H NMR and ^{13}C NMR signals* of undecenyl resorc[4]arene **1b** (*cone*)

| Carbon	^{13}C	^{1}H
C=O	172.5	-
C_{Ar}–O	156.2	-
=CH	139.3	5.82 ddt (17.2, 10.2, 6.5)
CH_i (25,26,27,28)	126.0	6.51 s
C_{Ar}–C	124.2	-
=CH_2	114.3	4.99 br d (17.2)
		4.93 br d (10.2)
CH_e (5,11,17,23)	96.4	6.30 s
OCH_2	64.4	3.95 t (6.8)
OMe	56.0	3.63 s
CH_2-(CO)	39.2	2.83 d (7.6)
CH_2-(CH=)	34.0	2.03 m (6.5)
CH	33.2	4.96 t (7.6)
CH_2-(CH_2-CH=)	29.1	1.35 br m
CH_2-(CH_2O)	28.8	1.49 br m
$CH_2 \times 5$	29.7	1.27 br m
	29.6	
	29.5	
	29.3	
	26.0	

* 600 MHz (^{1}H) and 100 MHz (^{13}C), CDCl$_3$, T = 300 K; coupling constants J (Hz) are given in parentheses.

Table 3S. ^{1}H NMR and ^{13}C NMR signals* of undecenyl resorc[4]arene **1c** (*1,2-alternate*)

Carbon	^{13}C	^{1}H
C=O	172.7 × 2 172.3 172.2	-
C_{Ar}–O (6,22) C_{Ar}–O (4,24) C_{Ar}–O (10,18) C_{Ar}–O (12,16)	156.4 156.3 156.1 156.1	-
=CH	139.2	5.79 ddt (17.2, 10.2, 6.5)
CH_i (25,28) CH_i (26,27)	127.6 126.5	7.25 s 6.36 s
C_{Ar}–C (7,21) C_{Ar}–C (1,3) C_{Ar}–C (13,15) C_{Ar}–C (9,19)	124.7 124.4 124.0 123.4	-
=CH_2	114.4	4.97 br d (17.2) 4.91 br d (10.2)
CH_e (11,17) CH_e (5,23)	96.7 96.0	6.38 s 6.40 s
OCH_2 (2) OCH_2 (14) OCH_2 (8,20)	64.4 63.1 64.4 × 2	4.00 t (7.0) 3.97 t (7.0) 3.91 t (7.0)
OMe	56.4 56.1 55.9 55.9	3.83 s 3.82 s 3.75 s 3.64 s
CH_2-(CO) (2) CH_2-(CO) (14) CH_2-(CO) (8,20)	41.2 40.3 39.4 × 2	2.87 d (8.0) 2.33 d (8.0) 2.88 dd (15.1)
CH_2-(CH=)	34.0	2.03
CH (2) CH (14) CH (8,20)	34.0 33.6 34.0 × 2	5.46 t (8.0) 5.10 t (8.0) 5.06 dd (9.6, 6.5)
CH_2-(CH_2-CH=)	29.1	1.38 br m
CH_2-(CH_2O)	28.8	1.45 br m
CH_2 × 5	29.7 29.7 29.7 29.6 26.0	1.27 br m

* 600 MHz (^{1}H) and 100 MHz (^{13}C), CDCl$_3$, T = 300 K; coupling constants J (Hz) are given in parentheses.

Figure 1S. Perspective views of the self-assembly of resorc[4]arene **1a** in the crystal lattice through hydrophilic and hydrophobic layers, with approximate thickness of the layers: (a) front view; (b) side view. Colors are as follows: C, grey; O, red. Hydrogen atoms are omitted for clarity.
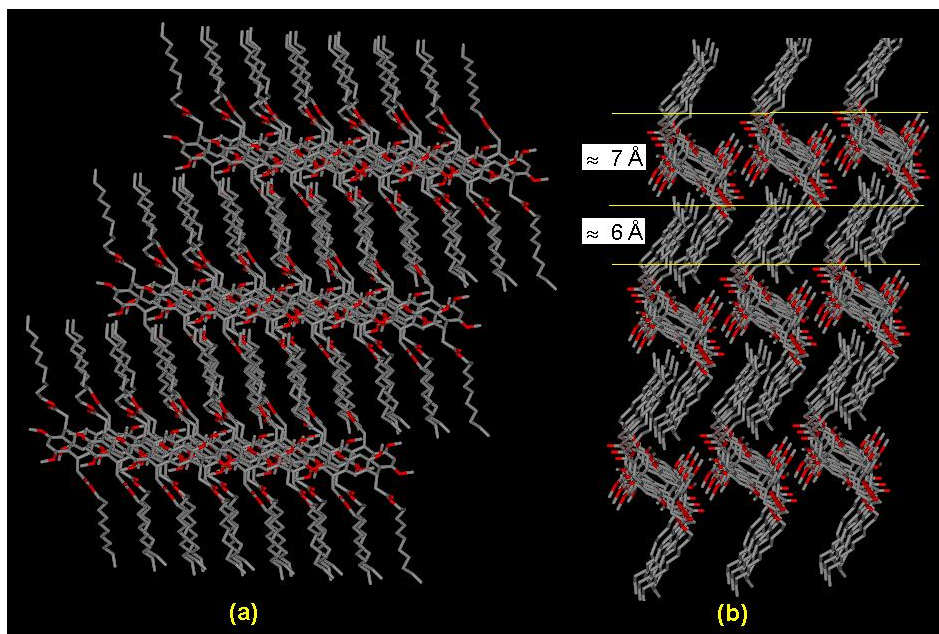
Crystal data, data collection and refinement parameters for resorc[4]arene **1a**

Chemical formula	$C_{88}H_{128}O_{16}$
Formula weight	1441.97
crystal system	triclinic
space group	*P1*
a (Å)	12.297(5)
b (Å)	17.946(5)
c (Å)	10.559(5)
α (°)	100.610(5)
β (°)	102.440(5)
γ (°)	105.110(5)
V (Å^3)	2124(1)
Z	1
ρ_{calcd} (g × cm^{-3})	1.127
μ (mm^{-1})	0.6 (Cu-K$_\alpha$)
Data Collection and Refinement	
2θ max for data collection (°)	139.98
Temperature (K)	293
Data collected (*h, k, l*)	(-14, -21, -12) to (14, 21, 12)
Total reflections	8039
Unique reflections	7989 (R$_{int}$ = 0.0)
Observed reflections	2598 [*F*o>4.0σ(*F*o)]
Goodness-of-fit S on F^{2} [a]	1.040
Final R indices (obs. data)[b]	R_1 = 0.0639, wR_2 = 0.143
Largest diff. peak and hole (e/Å^{-3})	0.16/-0.12

[a] Goodness-of-fit S = $[\Sigma w(Fo^2\text{-}Fc^2)^2/(n\text{-}p)]^{1/2}$, where *n* is the number of reflections and *p* the number of parameters. [b]R_1 = Σ || *F*o|-|*F*c||/Σ|*F*o|, wR_2 = $[\Sigma w(Fo^2\text{-}Fc^2)^2/\Sigma wFo^4]^{1/2}$.

Intensity data and cell parameters were recorded at room temperature (293 K) on a Siemens AED diffractometer using graphite monochromated Cu-K$_\alpha$ radiation. The intensities were corrected for Lorentz, polarization but not for absorption effects. This structure was characterized by poor diffraction, and several data collections carried out with different samples obtained from different crystallization methods always gave the same results.

The structure was solved by Direct methods using SIR2004 [1S] and refined on F_o^{2} by full-matrix least-squares procedures, using SHELXL-97 [2S]. The structure of the macrocycle is pseudo-centrosymmetric. The resorc[4]arene basket is centrosymmetric, but the terminal ester chains are non-centrosymmetric. All the non-hydrogen atoms were refined with anisotropic atomic displacements excepting 15 carbon atoms of the long aliphatic chains which were refined with isotropic atomic displacements. The hydrogen atoms were included in the refinement at idealized geometry (C-H 1.0 Å) and refined "riding" on the corresponding parent atoms.

Molecular geometry calculations were carried out using the PARST97 program [3S].

Figure 2S. Structures of the second-generation Grubbs (left) and Grubbs-Hoveyda (right) catalysts.
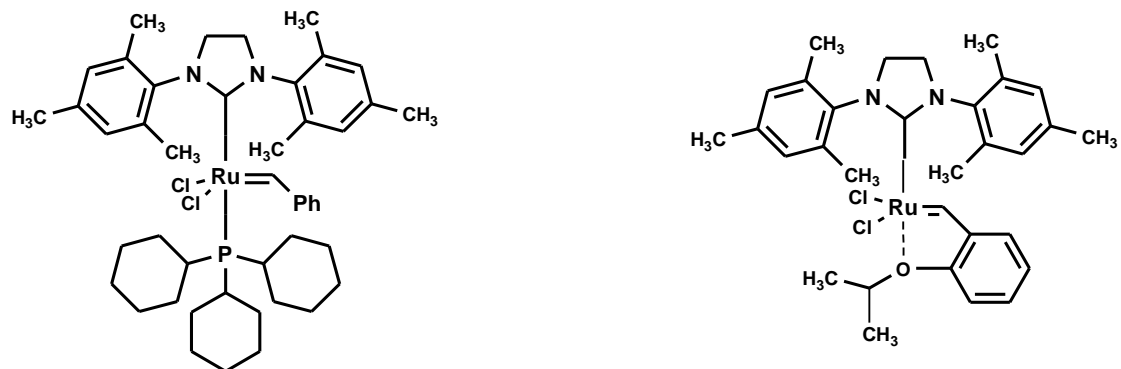
Table 4S. ^{1}H NMR and ^{13}C NMR signals* of bicyclic alkene **2a**

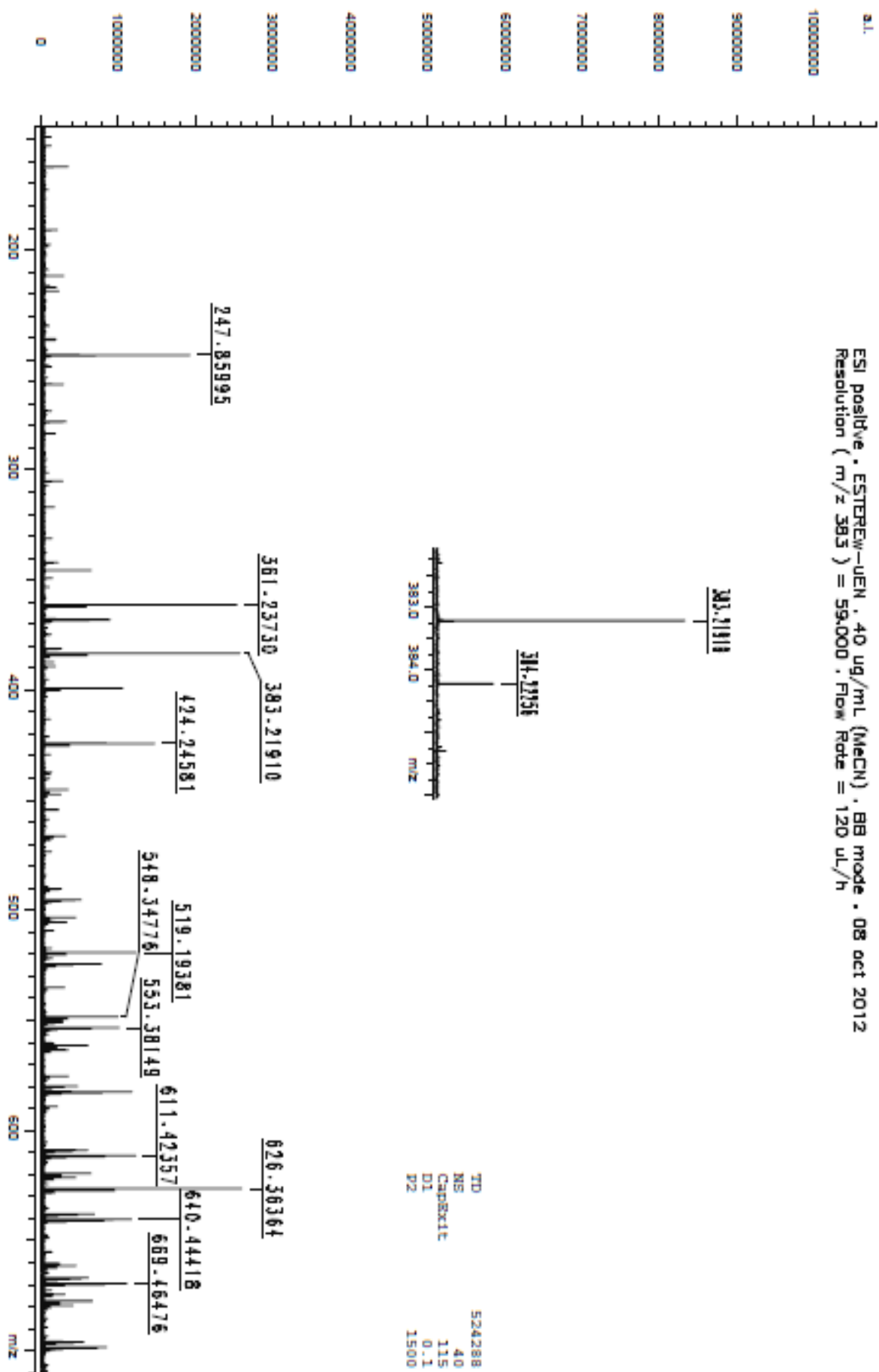| Carbon	^{13}C	^{1}H
C=O	172.5	-
C_{Ar}–O	156.5	-
	155.6	
CH= (*trans*)	130.8	5.34 br t (3)
CH= (*cis*)	[130.1]	[5.32 br t (4)]
CH$_i$ (26,28)	126.3	6.17 br s
		[6.18 br s]
CH$_i$ (25,27)	125.3	6.84 br s
		[6.85 br s]
C_{Ar}–C	125.3	-
	122.6	
CH$_e$ (5,17)	97.4	6.48 s
CH$_e$ (11,23)	95.5	6.40 s
OCH$_2$	64.3	3.95 dd (11.5, 7)
		3.89 m
OMe	56.1	3.64 s
	55.9	3.90 s
CH$_2$-(CO)	39.7	2.69 dd (14.5, 7)
		2.64 dd (14.5, 7)
CH$_2$-(CH=)	32.0	2.01 m
	[26.8]	[2.03 m]
CH	32.8	5.05 t (7)
CH$_2$-(CH$_2$-CH=)	28.9	1.35 m
CH$_2$-(CH$_2$O)	28.6	1.50 m
CH$_2$ × 5	29.5	1.24 br m
	29.3	
	29.1	
	28.1	
	25.9	

* 600 MHz (^{1}H) and 100 MHz (^{13}C), CDCl$_3$, T = 300 K; coupling constants J (Hz) are given in parentheses. Proton and carbon resonances for the *cis* form, not coincident or overlapped by those of the *trans* form, are indicated by square brackets.

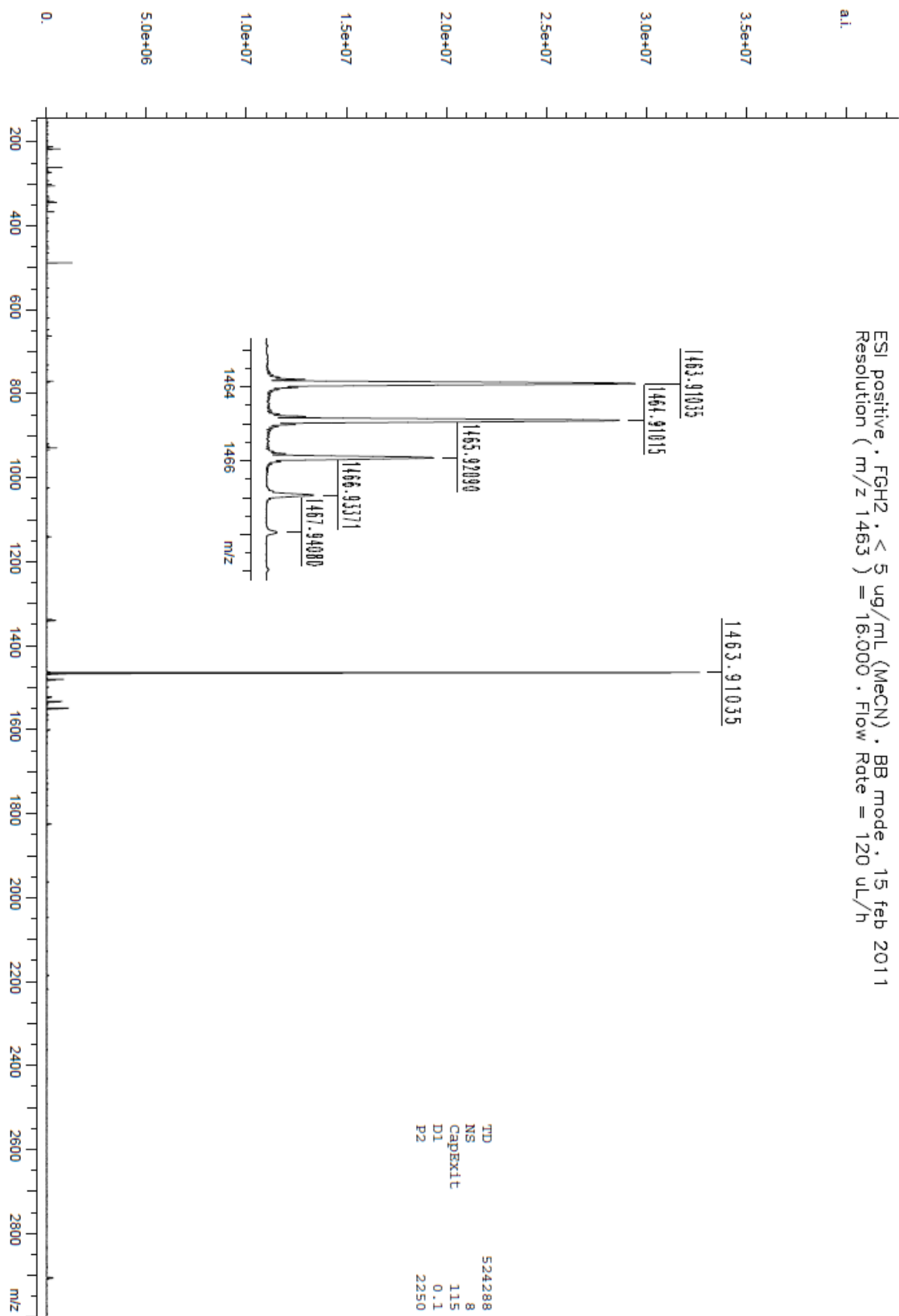**Table 5S.** ^{1}H NMR and ^{13}C NMR signals* of linear dimer **3a**

Carbon	^{13}C	^{1}H
C=O	172.5	-
C$_{Ar}$–O	156.5	-
	155.6	
CH= (*trans*)	130.8	5.33 tt (3,1)
CH= (*cis*)	130.3	5.38 tt (3,1)
	[130.1]	[5.35 m]
	[129.8]	[5.36 m]
CH$_i$ (26,28)	126.3	6.18 br s
CH$_i$ (25,27)	125.3	6.87 br s
C$_{Ar}$–C	125.3	-
	122.6	
CH$_e$ (5,17)	97.4	6.49 s
CH$_e$ (11,23)	95.5	6.41 s
OCH$_2$	64.3	3.92 m
		3.87 m
OMe	56.1	3.60 s
	55.9	3.88 s
CH$_2$-(CO)	39.7	2.67 m
CH$_2$-(CH=)	32.6	1.96 m
	32.0	2.02 m
	[26.7]	[2.03 m]
	[26.8]	[2.03 m]
CH	32.8	5.04 t (7.5)
CH$_2$-(CH$_2$-CH=)	29.4	1.32 m
	28.9	1.35 m
CH$_2$-(CH$_2$O)	28.6	1.50 m
CH$_2$ × 5	29.5	1.24 br m
	29.3	
	29.1	
	28.1	
	25.9	

* 600 MHz (^{1}H) and 100 MHz (^{13}C), CDCl$_3$, T = 300 K; coupling constants J (Hz) are given in parentheses. Proton and carbon resonances for the *cis* form, not coincident or overlapped by those of the *trans* form, are indicated by square brackets.
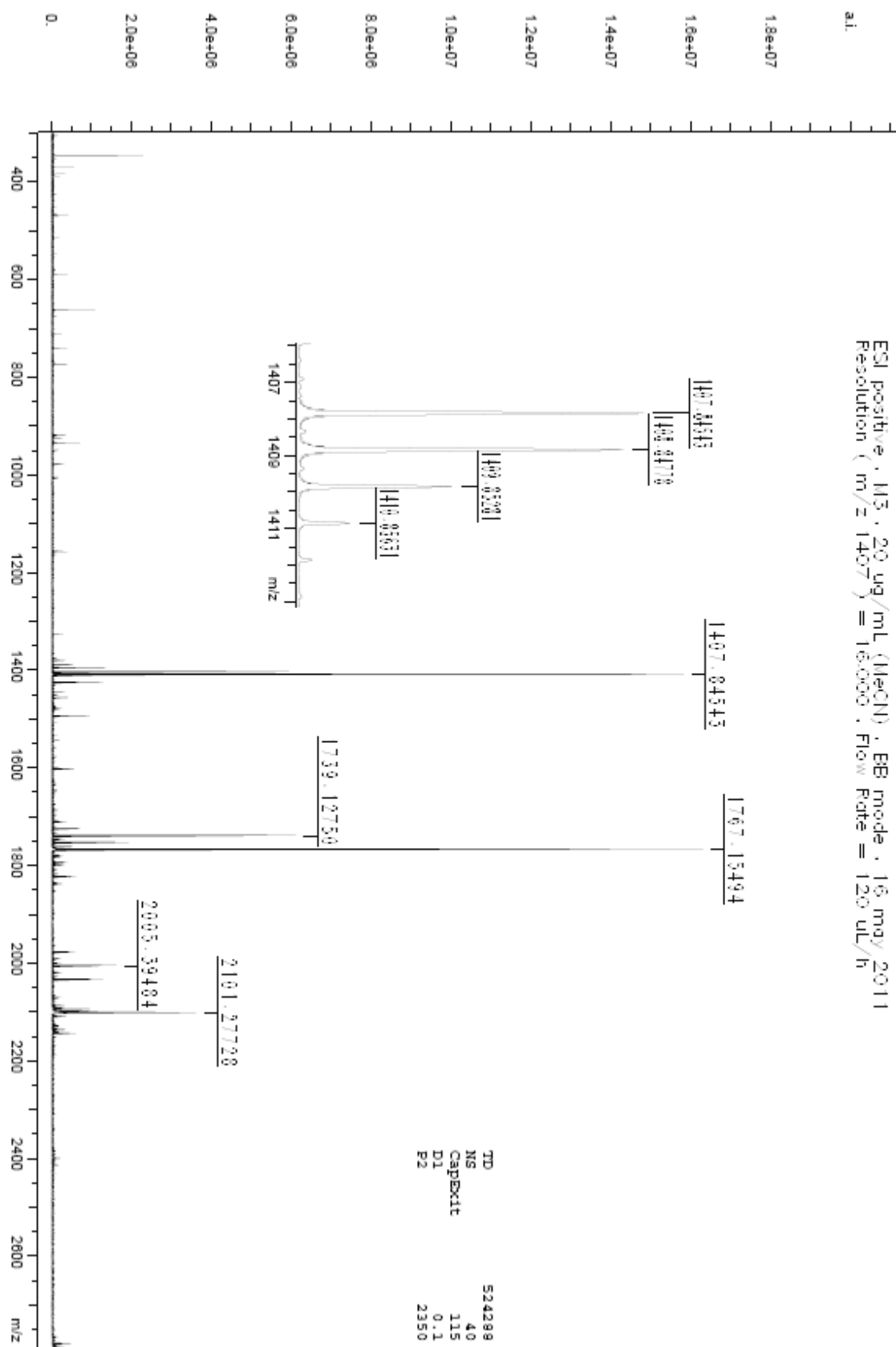
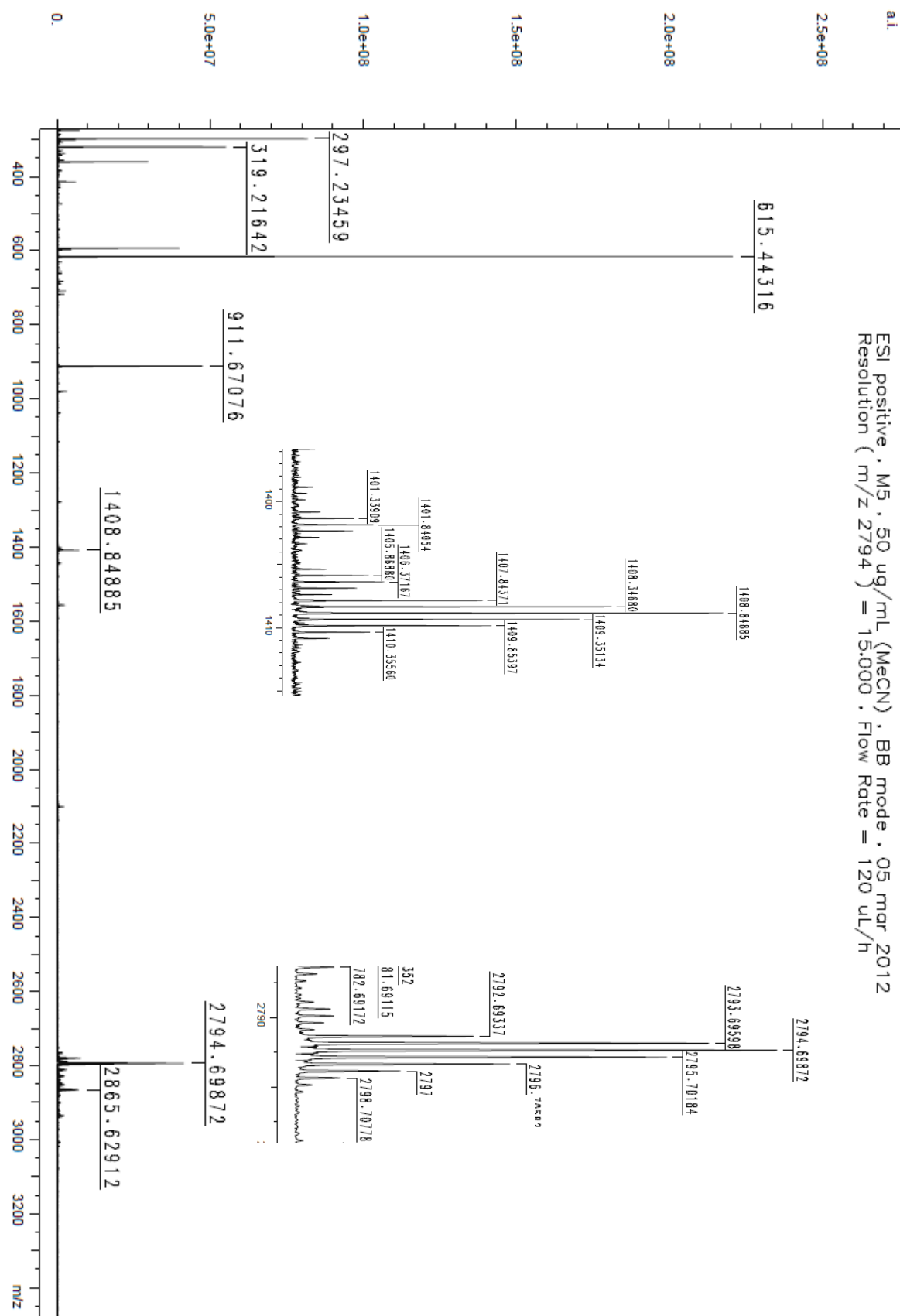**ESI-HRMS spectrum of ω-undecenyl (*E*)-2,4-dimethoxycinnamate.** Solvent: MeCN (40 ppm)

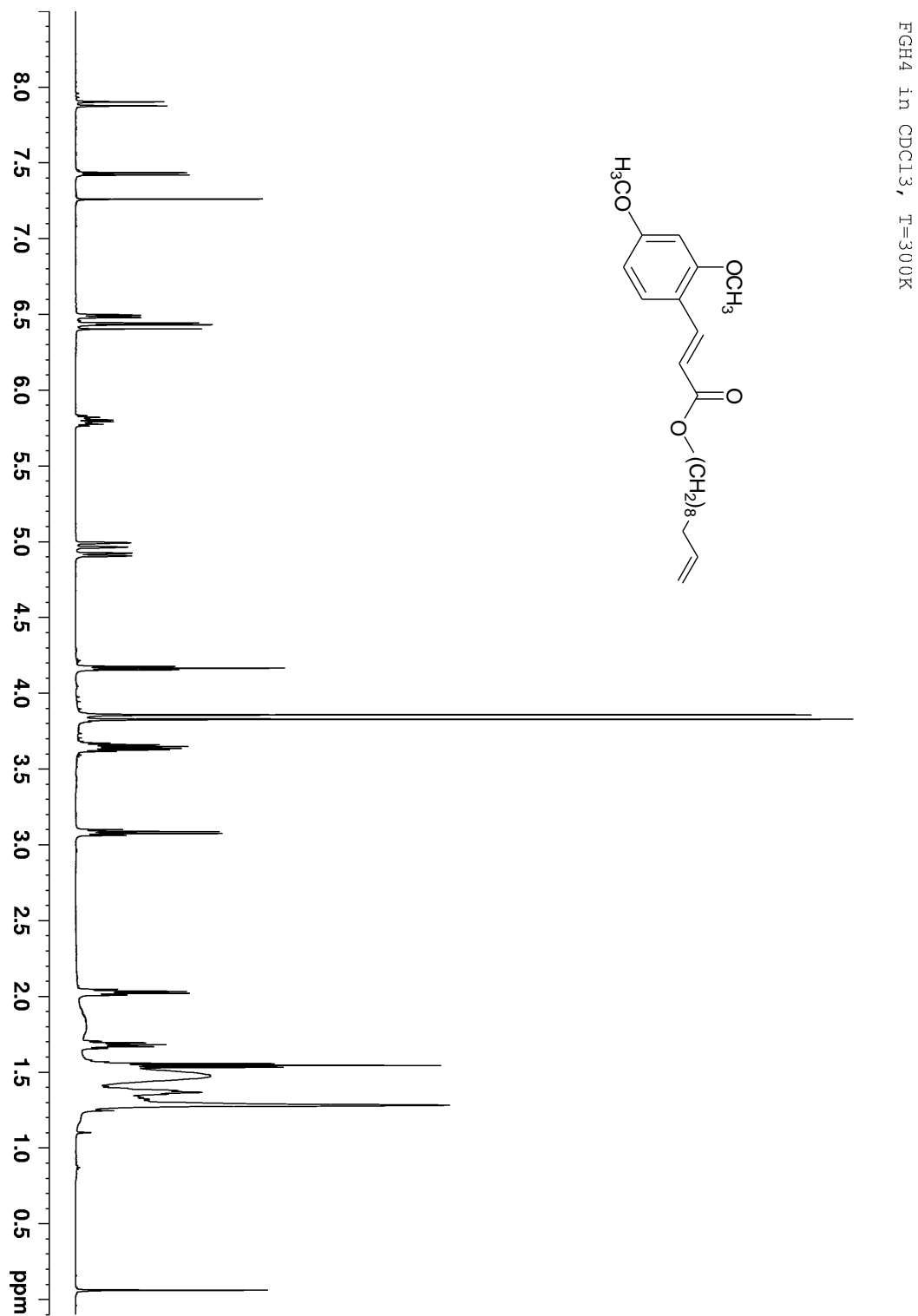**ESI-HRMS spectrum of undecenyl resorc[4]arenes 1a–1c**. Solvent: MeOH (5 ppm)

ESI positive, FGH2, < 5 ug/mL (MeCN), BB mode, 15 feb 2011
Resolution (m/z 1463) = 16.000, Flow Rate = 120 uL/h

TD	524288
NS	8
CapExit	115
D1	0.1
P2	2250

Peaks: 1463.91035, 1464.91015, 1465.92090, 1466.93371, 1467.94080

ESI-HRMS spectrum of bicyclic alkene 2a. Solvent: MeCN (20 ppm)

ESI-HRMS spectrum of linear dimer 3a. Solvent: MeCN (30 ppm)

ESI positive, M5, 50 ug/mL (MeCN), BB mode, 05 mar 2012
Resolution (m/z 2794) = 15.000, Flow Rate = 120 uL/h

615.44316

319.21642

297.23459

911.67076

1408.84885

1401.33909
1401.84054
1405.86880
1406.37167
1407.84371
1408.34880
1408.84885
1409.35134
1409.85397
1410.35560

2792.69337
2793.69598
2794.69872
2795.70184
2796.70583
2798.70778
2865.62912

781.69115
782.69172

^{1}H NMR spectrum of ω-undecenyl (*E*)-2,4-dimethoxycinnamate. 600 MHz, CDCl$_3$, 300 K

^{13}C NMR spectrum of ω-undecenyl (E)-2,4-dimethoxycinnamate. 100 MHz, CDCl$_3$, 300 K
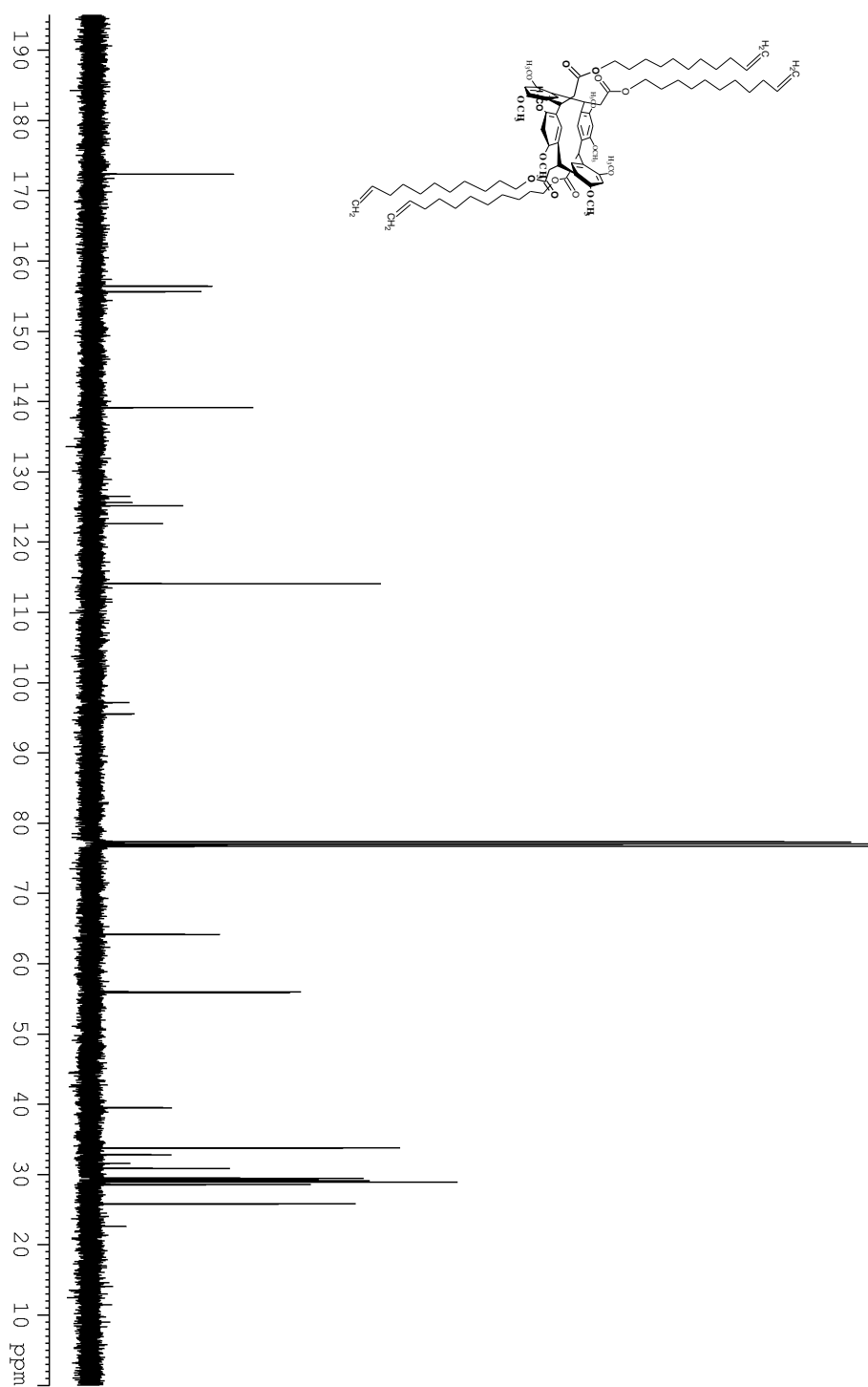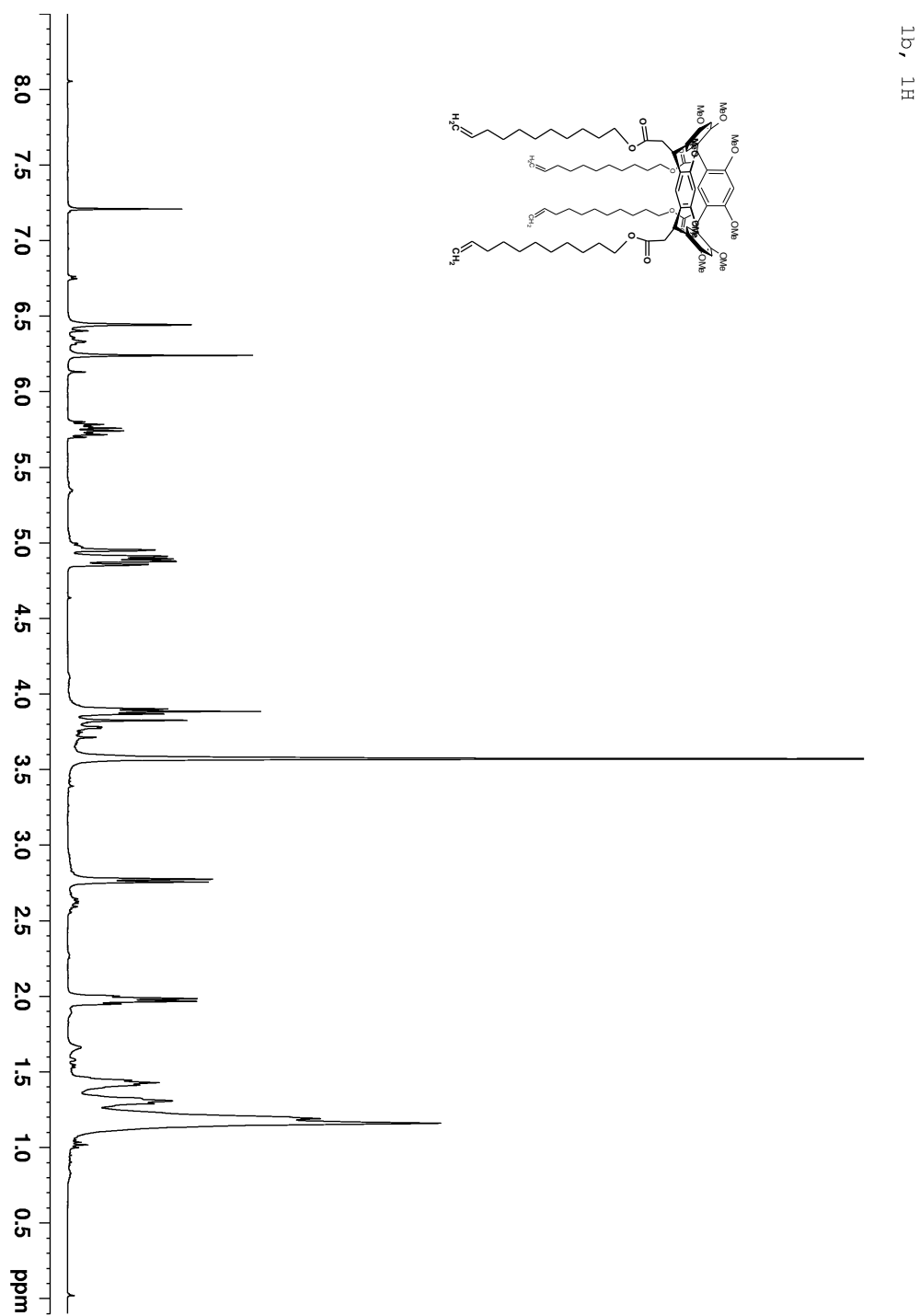

13C FGH4 in CDC13

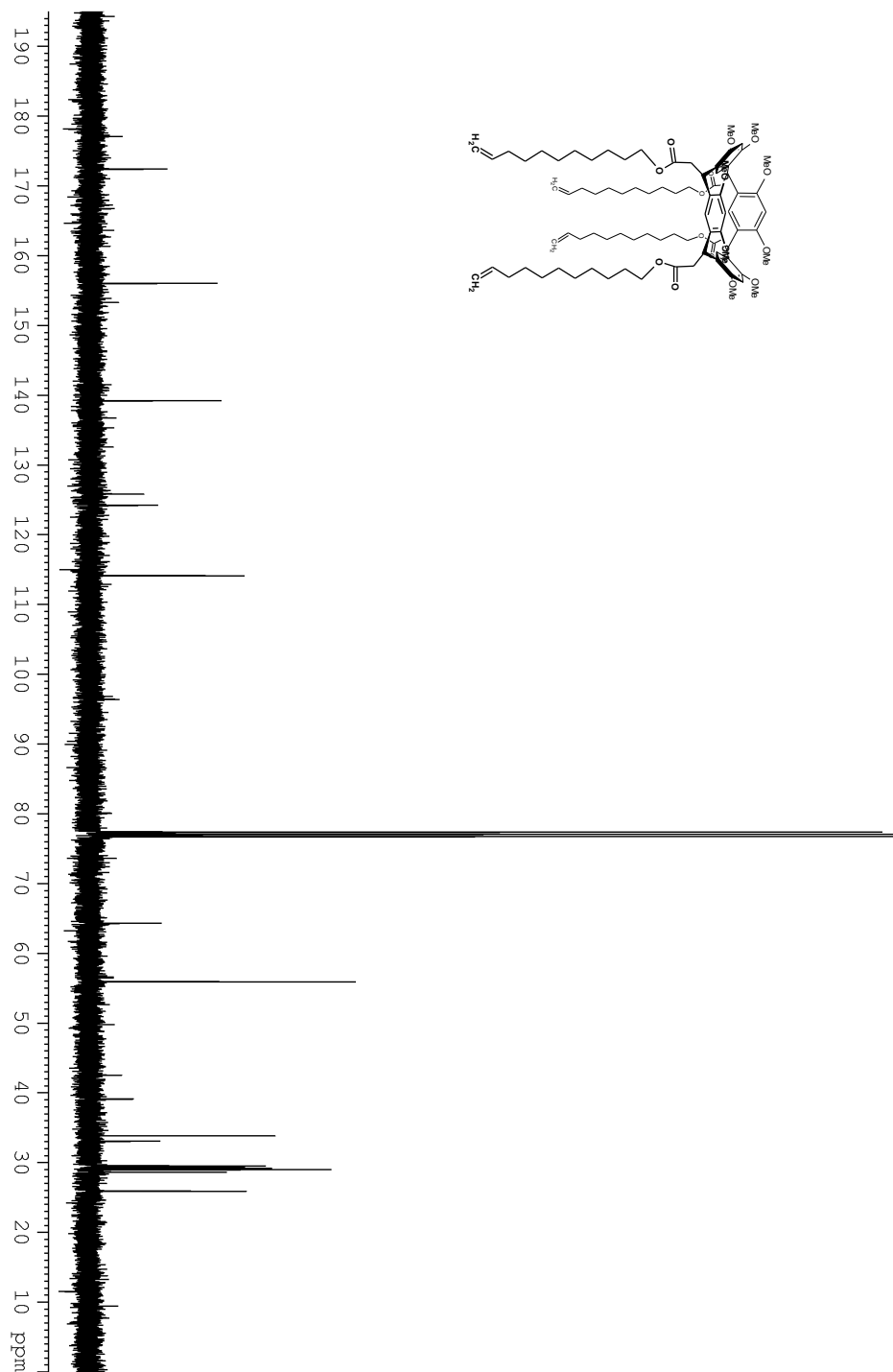**¹H NMR spectrum of undecenyl resorc[4]arene 1a (*chair*).** 600 MHz, CDCl₃, 300 K
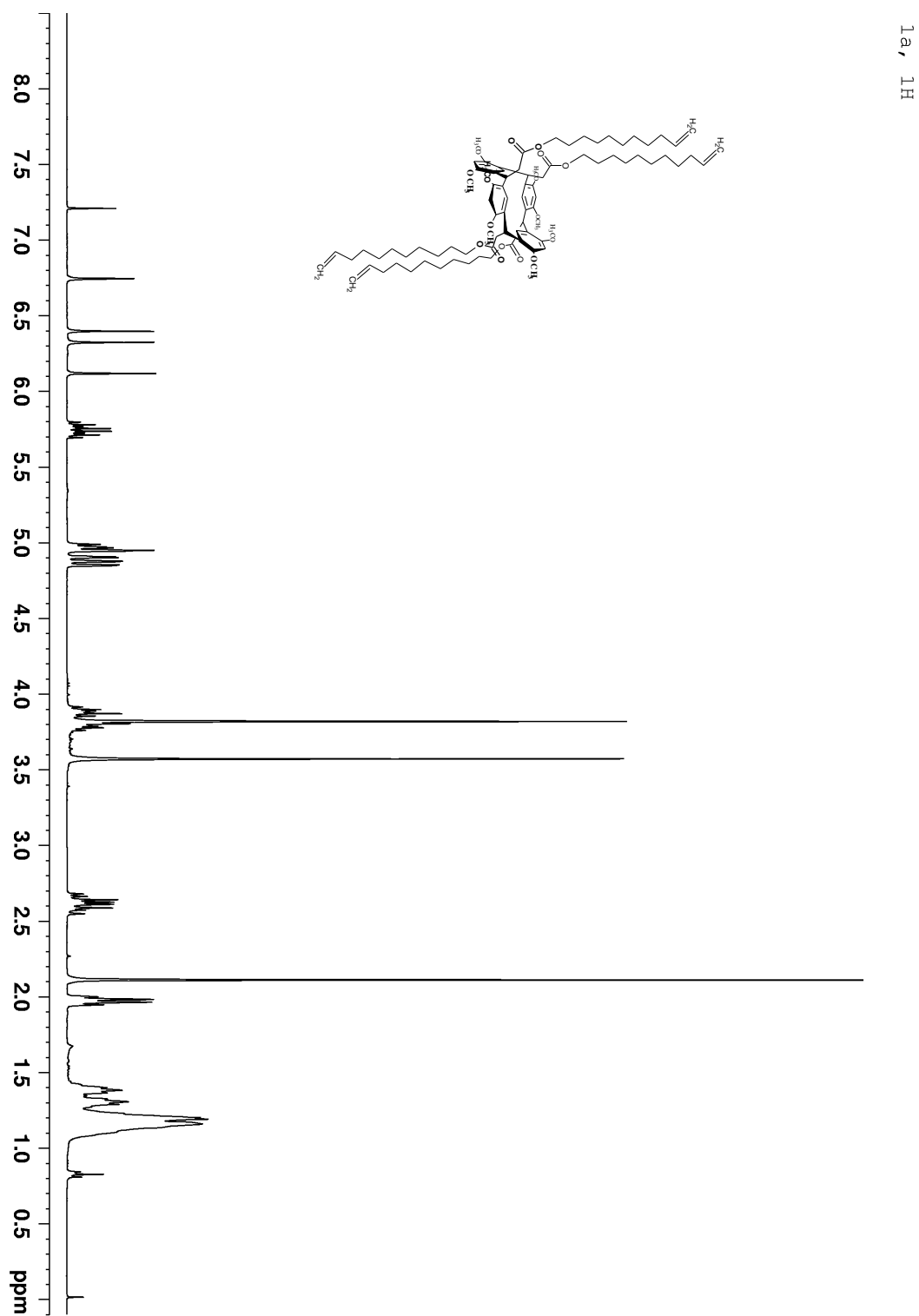
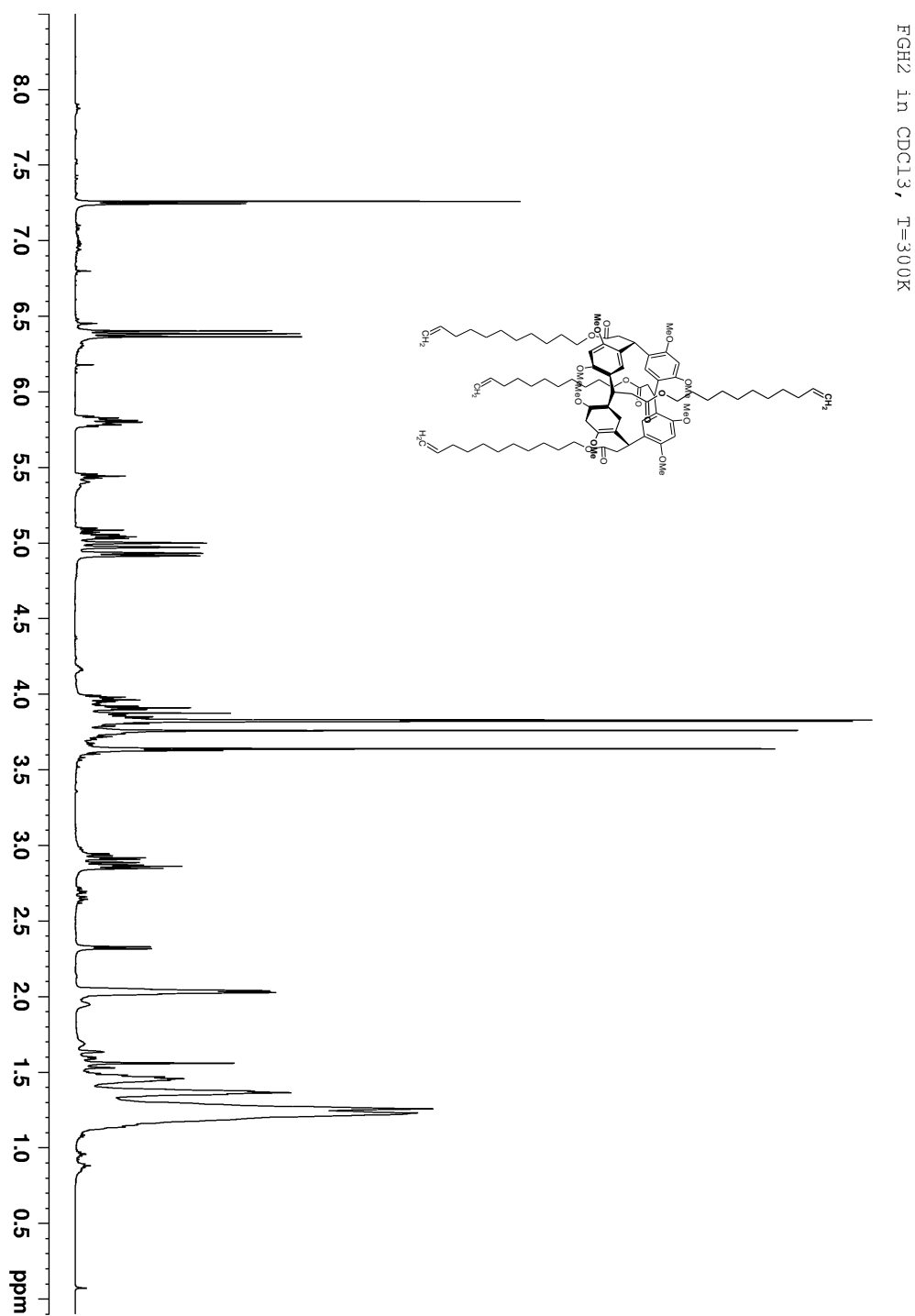**^{13}C NMR spectrum of undecenyl resorc[4]arene 1a (*chair*).** 100 MHz, CDCl$_3$, 300 K

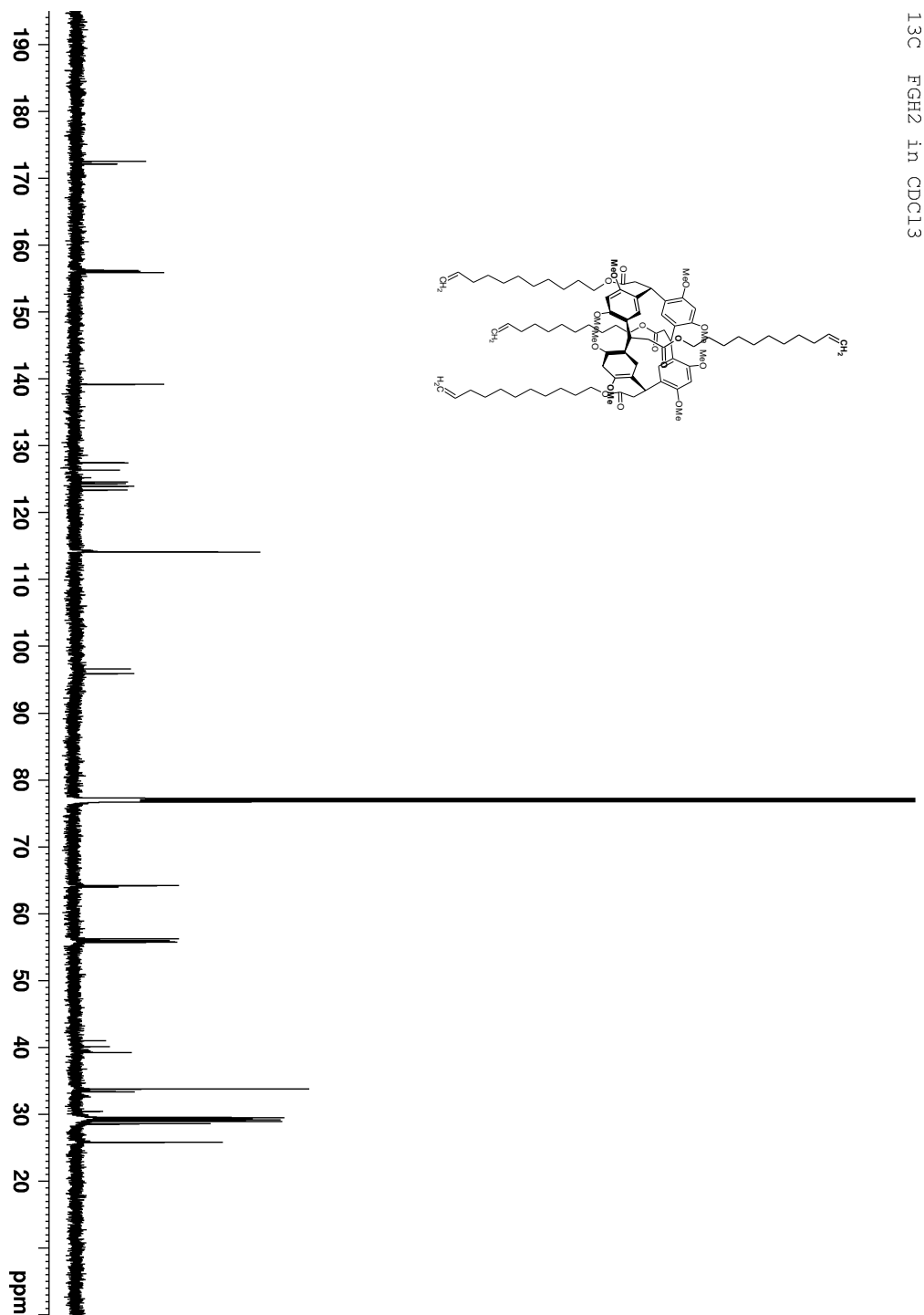**¹H NMR spectrum of undecenyl resorc[4]arene 1b (*cone*).** 600 MHz, CDCl₃, 300 K

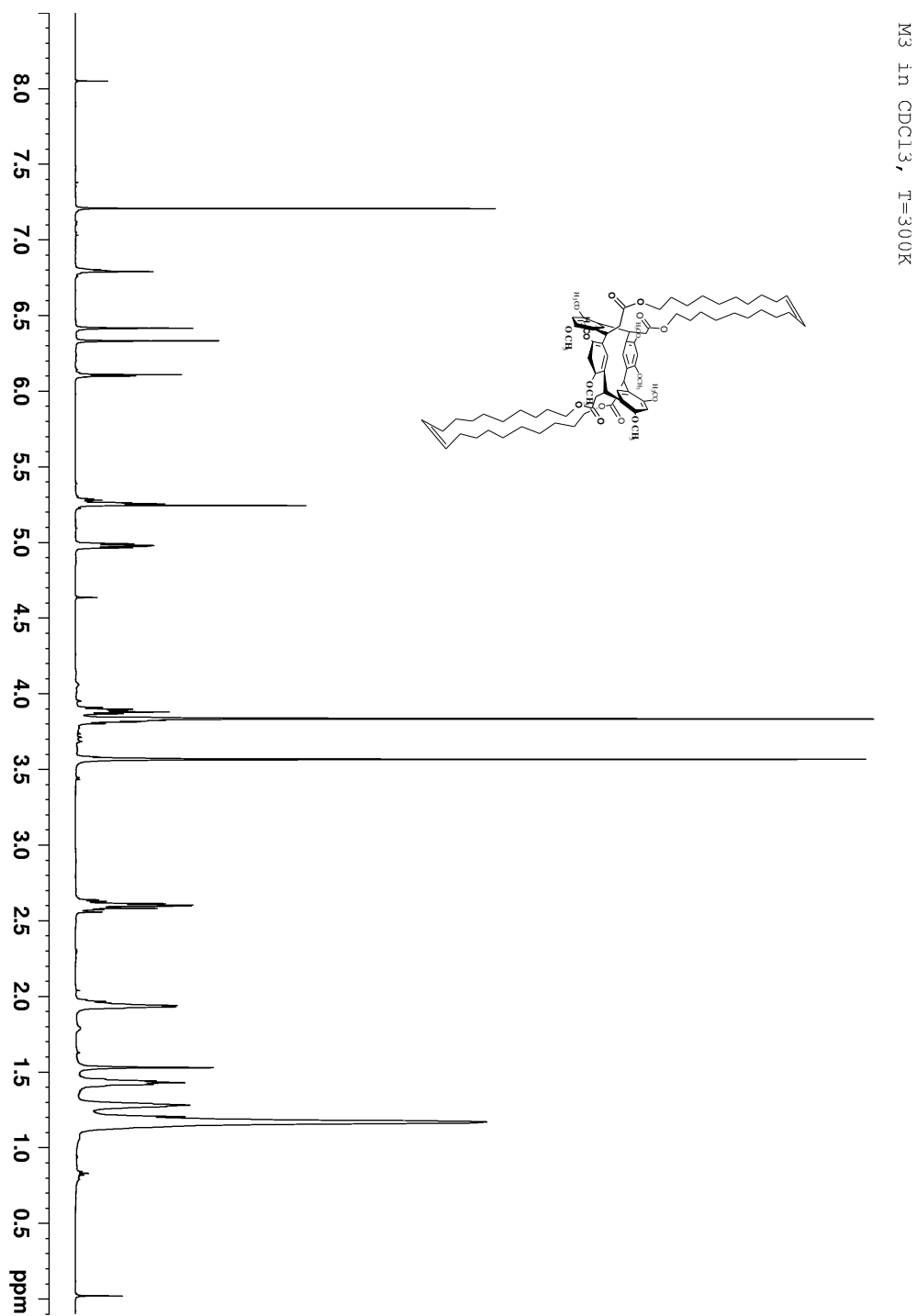**^{13}C NMR spectrum of undecenyl resorc[4]arene 1b (*cone*).** 100 MHz, CDCl$_3$, 300 K

¹H NMR spectrum of undecenyl resorc[4]arene 1c (*1,2-alternate*). 600 MHz, CDCl₃, 300 K

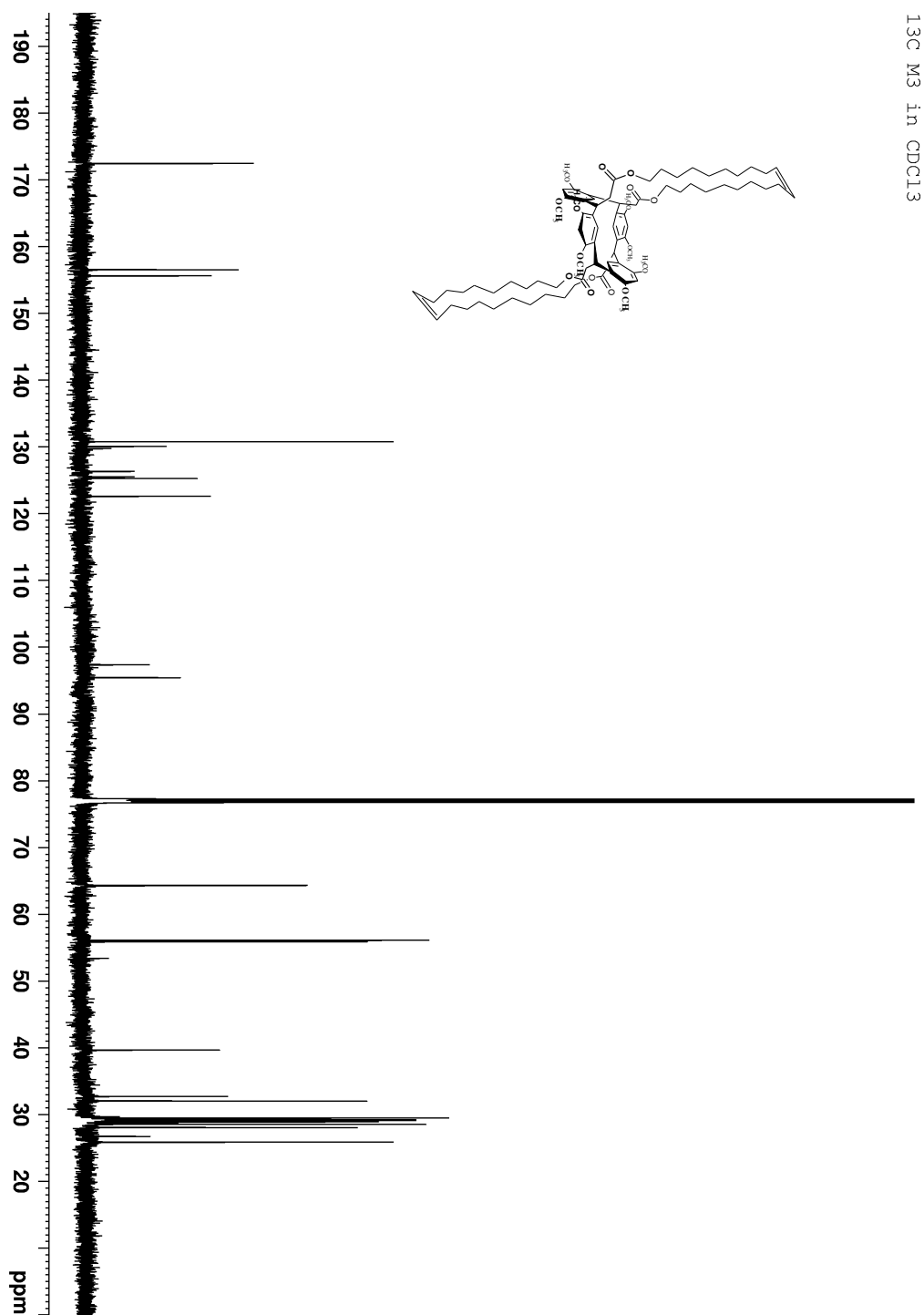**^{13}C NMR spectrum of undecenyl resorc[4]arene 1c (*1,2-alternate*).** 100 MHz, CDCl$_3$, 300 K

^{1}H NMR spectrum of bicyclic alkene 2a. 600 MHz, CDCl$_3$, 300 K

M3 in CDCl3, T=300K

¹³C NMR spectrum of bicyclic alkene 2a. 100 MHz, CDCl₃, 300 K

2D NMR spectra of bicyclic alkene 2a (NOESY)

2D-NOESY , M3 in CDCl3
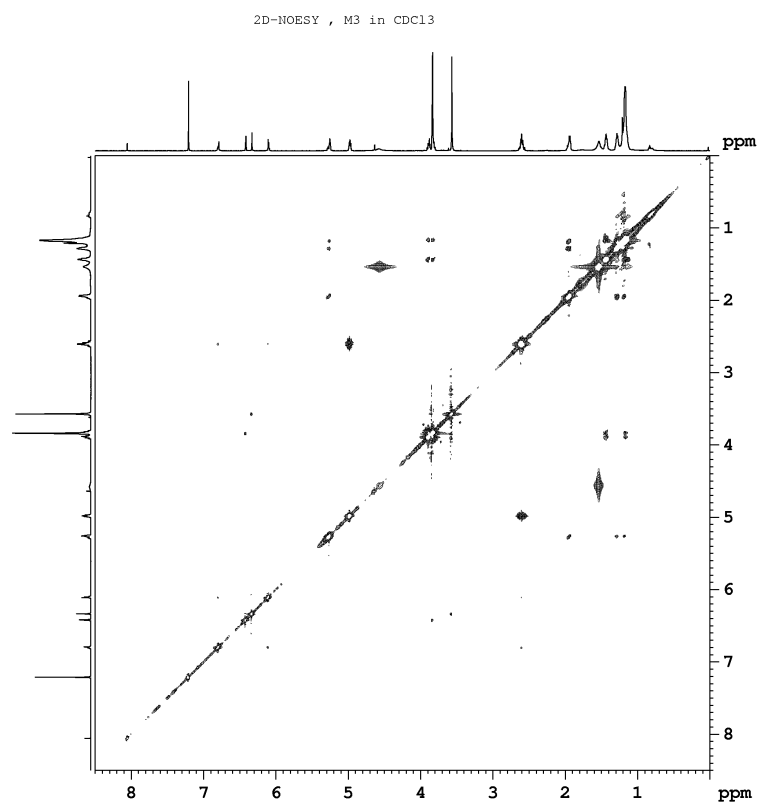
2D NMR spectra of bicyclic alkene 2a (TOCSY)

2D–TOCSY M3 in CDCl3
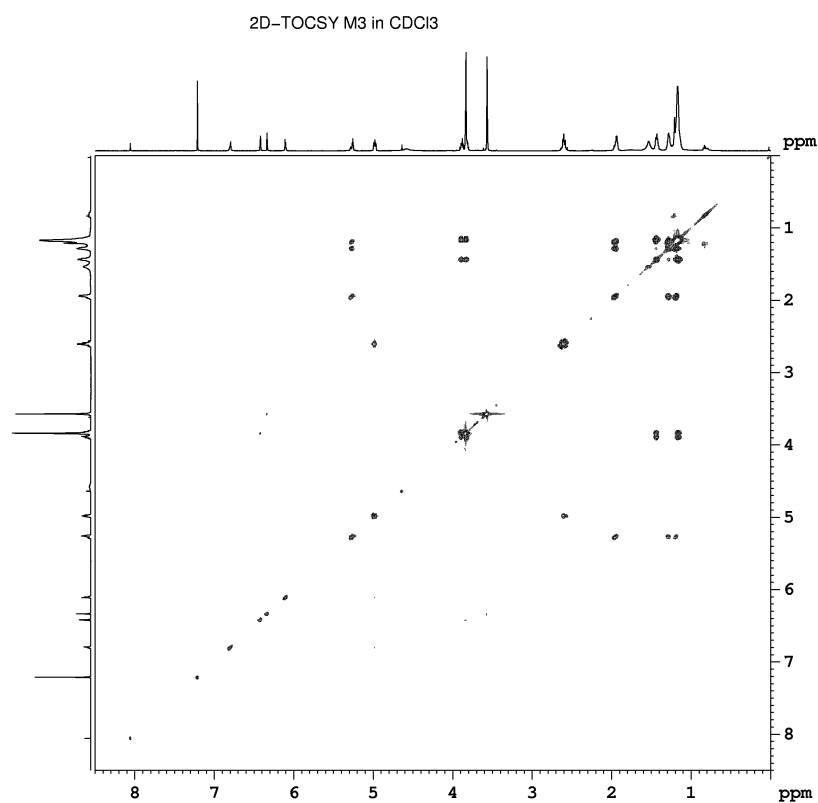
2D NMR spectra of bicyclic alkene 2a (HMBC)

HMBC, M3 in CDCl3
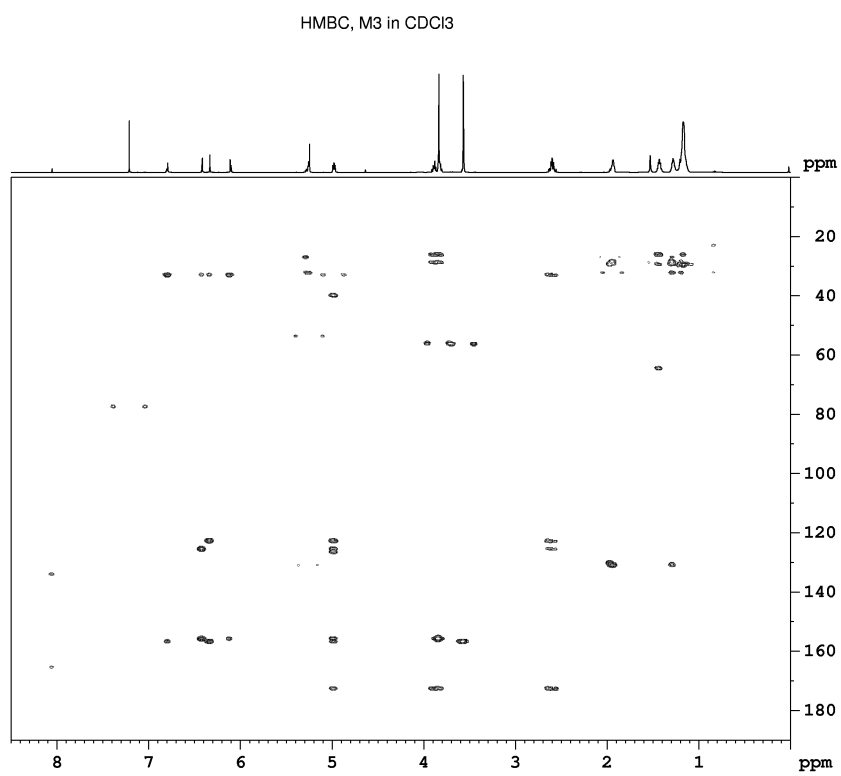
2D NMR spectra of bicyclic alkene 2a (HSQC)

HSQC M3 in CDCl3
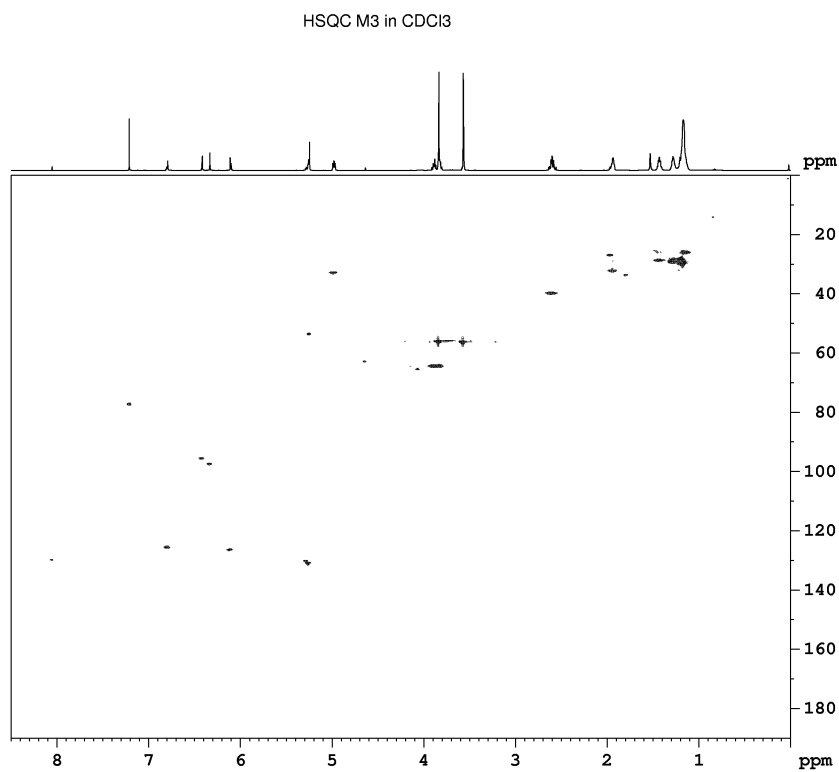
^{1}H NMR spectrum of linear dimer 3a. 600 MHz, CDCl$_3$, 300 K

M5 in CDCl3, T=301K
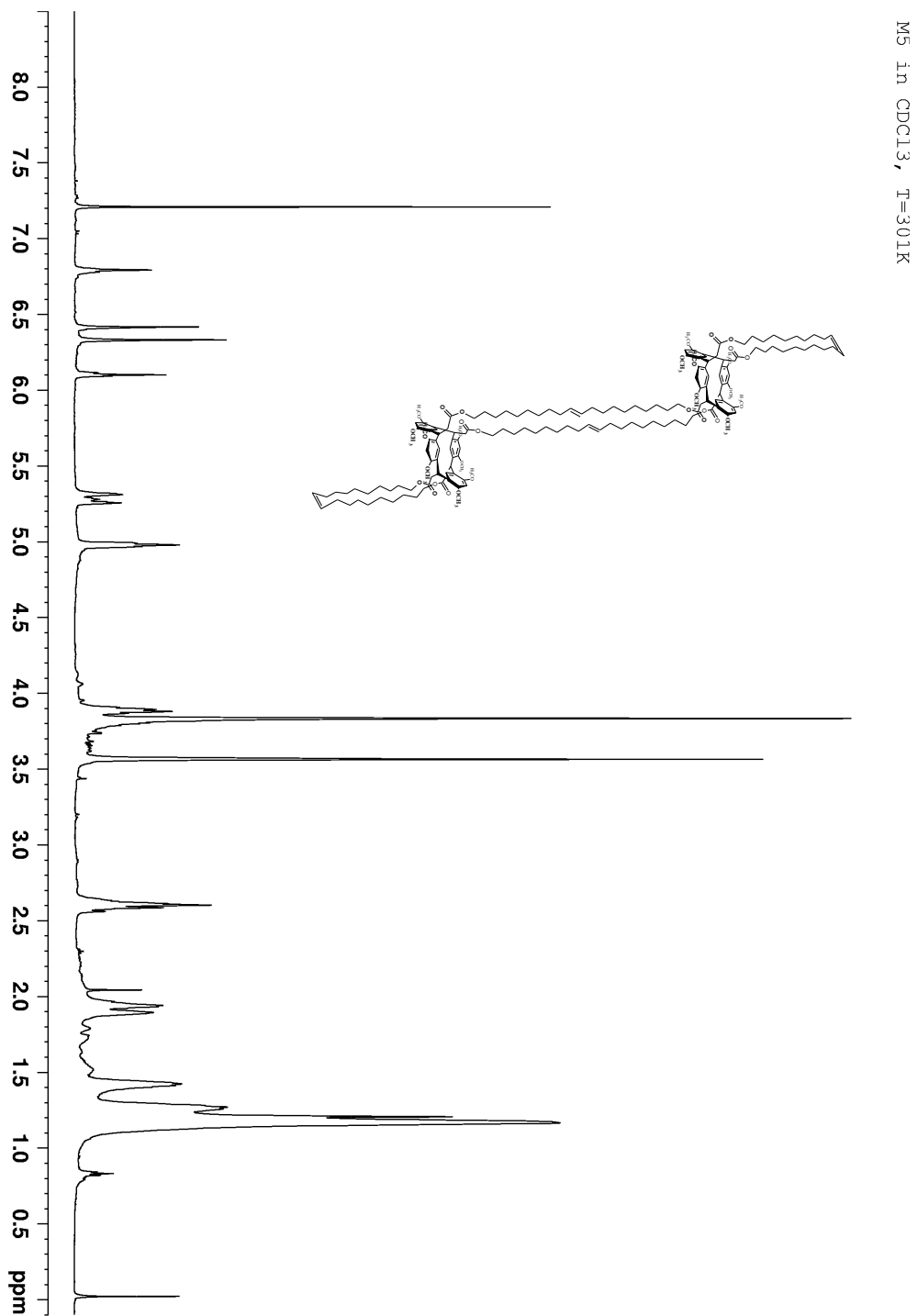
13C NMR spectrum of linear dimer 3a. 100 MHz, CDCl₃, 300 K

13C M5 in CDC13
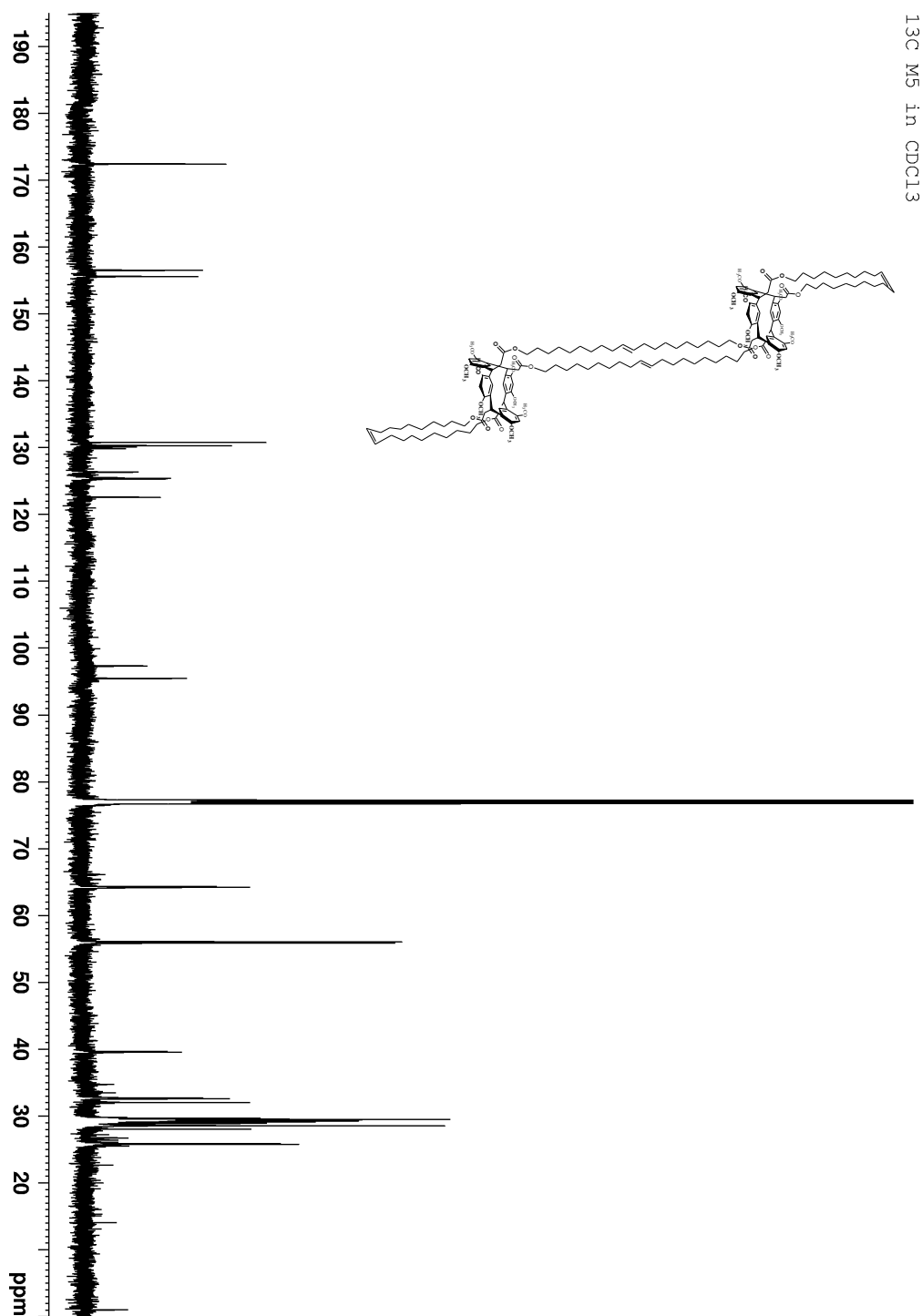
Figure 3S. FT-IR (KBr) spectrum of polymer **P1a**
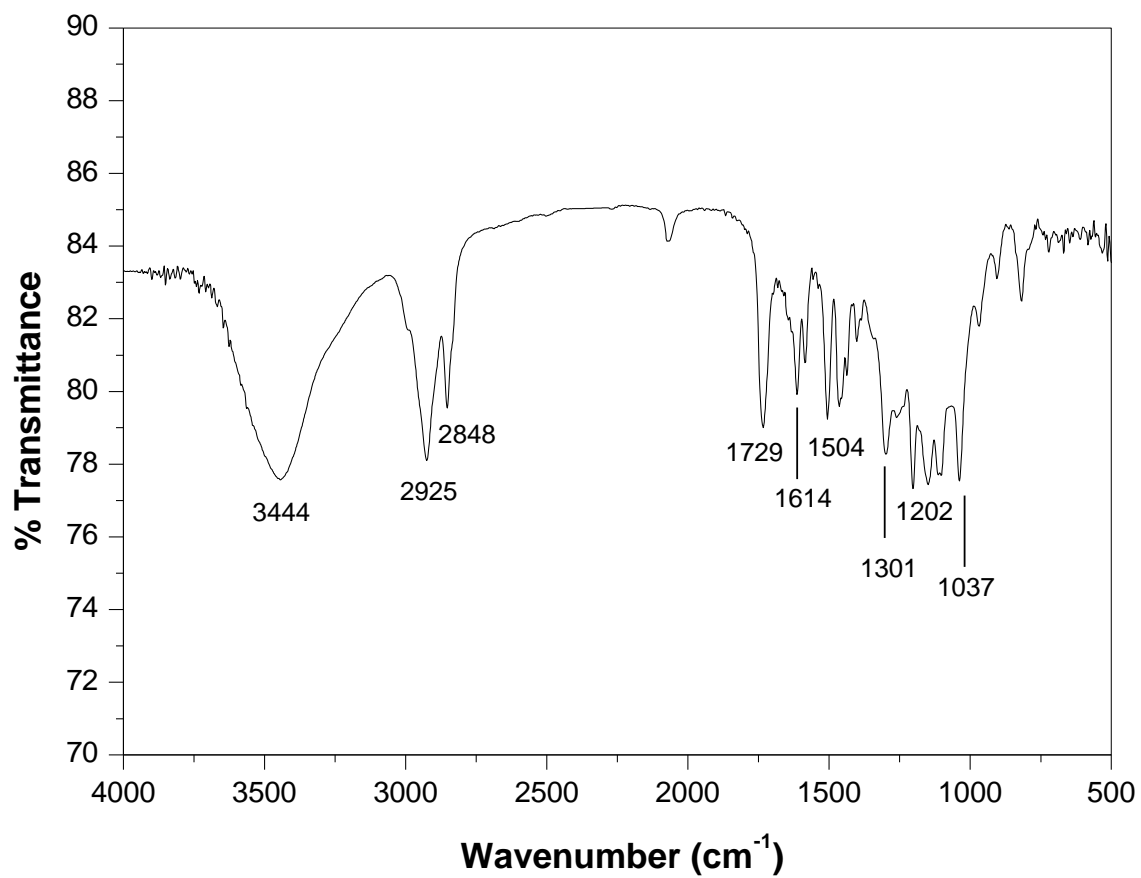
¹H NMR spectrum of compound 2ar. 400 MHz, CDCl₃, 300 K

15-07-2013 M3H2_CDCl3

Peaks:
- 7.260
- 6.809
- 6.453
- 6.387
- 6.211
- 5.054
- 5.035
- 5.017
- 3.925
- 3.909
- 3.872
- 3.641
- 2.709
- 2.689
- 2.672
- 2.649
- 1.506
- 1.492
- 1.272
- 1.256

Integrations:
- 0.456
- 0.492
- 0.498
- 0.458
- 0.931
- 5.363
- 2.987
- 1.990
- 2.581
- 0.569
- 26.917

^{13}C NMR spectrum of compound 2ar. 100 MHz, CDCl$_3$, 300 K

M.JH2. CDCl3. 15/07/2013

172.438
156.478
155.762
128.577
125.776
125.090
122.787
97.260
95.560
77.321
77.208
77.004
76.686
64.227
56.067
55.877
53.389
39.626
32.804
31.913
29.682
29.341
29.026
28.911
28.826
28.535
28.315
28.201
28.054
27.851
25.721
22.671
14.074

ESI-HRMS spectrum of compound 2ar. Solvent: MeCN (5 ppm)

ESI positive , FGH3 , < 5 ug/mL (MeCN) , BB mode , 16 feb 2011
Resolution (m/z 1411) = 16.000 , Flow Rate = 120 uL/h

1411.8772

TD	524288
NS	16
CapExit	115
D1	0.1
P2	2500

Peaks: 1411.8772, 1412.8759, 1413.8853, 1414.8930, 1415.8943
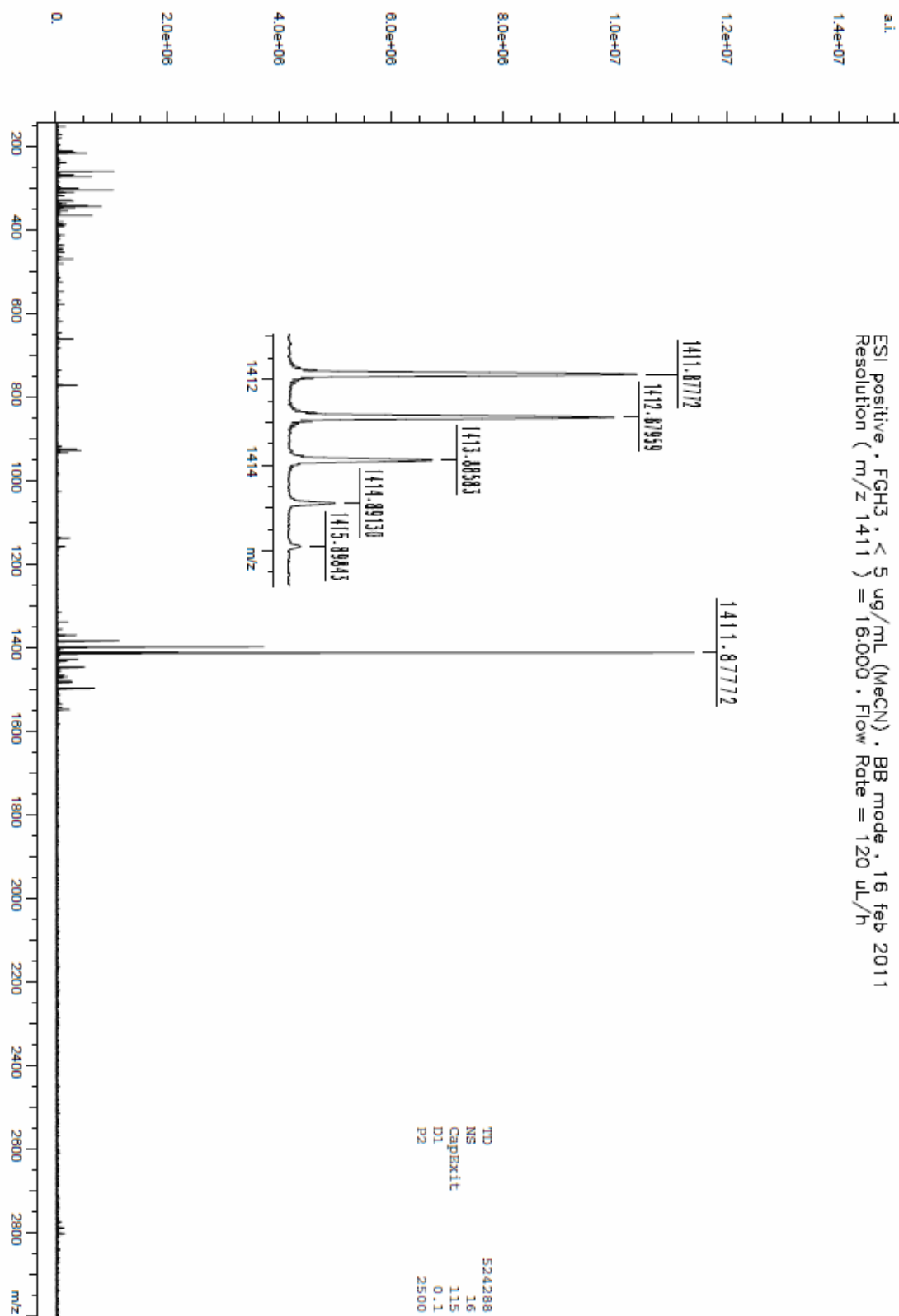
Computational methods

The Gaussian 09 program [4S] was used for the *ab initio* molecular orbital calculations. 6-311++G**, aug-cc-pVDZ, and aug-cc-pVTZ basis sets were used. Electron correlation energies were corrected by the second-order Møller-Plesset perturbation method (MP2) [5S,6S]. Geometries of isolated molecules were optimized at the MP2/6-311++G** level and were used for calculations of the interaction energies of the resorcinol-ethylene complexes. Basis set superposition error (BSSE) [7S] was corrected by the counterpoise method of Simon [8S] implemented in Gaussian 09.

Solid state ^{13}C CPMAS NMR spectroscopy

Solid state ^{13}C CPMAS NMR spectra were measured on a Bruker Avance III spectrometer at 100.63

MHz. Samples were packed into 4 mm zirconia rotors, and sealed with Kel-F caps. The spin rate was 8

kHz. The cross polarization (CP) was performed by applying the variable spin-lock sequence RAMP-

CPMAS [9S]; the RAMP was applied on the ^{1}H channel and during the contact time the amplitude of the

RAMP was increased from 50 to 100% of the maximum value. All the spectra were obtained at room

temperature, with a contact time optimized at 6 ms, the recycle delay being 3 s and acquired with a time

domain of 1024 data points, zero filled and Fourier transformed with a size of 4096 data points, applying

an exponential multiplication with a line broadening of 4 Hz. ^{13}C chemical shifts were referenced to

tetramethylsilane used as an external reference.

Cartesian coordinates (Å) for model complex (A)

Atom	x	y	z
C	12.80975546	7.92727560	−2.48757130
C	13.07512885	9.21075977	−2.93531044
C	10.84086326	9.53742799	−3.64278803
C	10.51593875	8.26766875	−3.19517152
H	12.37513845	11.03589065	−3.84890907
H	13.60283534	7.31041213	−2.11096439
C	12.15991417	11.90769951	−0.80208345
C	12.55617455	13.14785841	−0.48854505
H	12.89502659	11.15136291	−1.05662163
H	11.10374536	11.65923987	−0.80157900
H	13.61234336	13.39631806	−0.48904952
H	11.82106214	13.90419501	−0.23400684
C	11.50180137	7.49188163	−2.61063303
H	11.23559330	6.51847267	−2.24018296
C	12.12715346	10.04182272	−3.51362355
H	9.50816195	7.92602934	−3.33300270
O	14.35764536	9.60241465	−2.79797202
H	14.45453783	10.47908175	−3.12303608
O	9.83229912	10.29222692	−4.12255980
H	10.16714840	11.12764395	−4.39376885

Cartesian coordinates (Å) for model complex (B)

Atom	x	y	z
O	15.50029923	8.43747519	3.31149209
O	16.41789348	6.52219188	-1.00445420
H	17.30930860	6.33251802	-0.77423060
H	16.37139162	8.28123288	3.62833020
H	17.10095500	7.33929434	1.46239900
C	13.48373013	8.00317611	0.36827157
H	12.47762577	8.22342630	0.06026364
C	14.65611763	3.33267609	1.46310411
H	13.73470794	2.88026280	1.11037253
H	15.54406198	2.72273962	1.59586515
C	15.16280184	8.09719432	2.05156810
C	16.07405280	7.51184616	1.18350519
C	15.64883969	7.13733890	-0.08398995
C	14.36511074	7.41612113	-0.52278996
H	14.01155758	7.20447283	-1.51351402
C	13.85271046	8.32319004	1.66322353
H	13.16335567	8.73785342	2.37327512
C	14.69740663	4.64338660	1.73450031
H	13.81173440	5.25672563	1.60306204
H	15.61970666	5.09384516	2.08709898

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